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THE SPECTRUM OF TREBLY IONIZED CERIUM[1]

BY R. J. LANG[2]

Abstract

The spectrum of cerium has been photographed from λ3600 to λ500 Å by means of a two-meter grating of 30,000 lines per inch mounted in a vacuum spectrograph, using the vacuum spark and the spark in nitrogen as sources. An analysis of the spectrum of Ce IV results in the location of the 6S – 6P, 6P – 6D, 6P – 7S, 5D – 6P, 6P – 8S and possibly the 6P – 7D multiplets. The ionization potential is approximately 33 3 volts.

Introduction

Virtually nothing is known concerning the single-electron spectrum of cerium although several attempts have been made to locate some of the doublets which are expected to occur in the spectral region below 3000Å. Gibbs and White (3) gave a pair of lines having a separation of 4620 cm.$^{-1}$ which were thought to represent the main doublet 6S–6P. Both lines were later changed by these authors (4) and another pair in the close neighborhood of the former was given showing a separation of 4707 cm.$^{-1}$. This latter assignment was made independently by Badami (1) and is confirmed by the results here presented. However, the further analysis of the spectrum made by Badami does not correspond to the present work.

Experimental Procedure

The spectrum of cerium was photographed from λ3600 to λ500Å on a two-meter grating having 30,000 lines per inch mounted in a vacuum spectrograph, using the vacuum spark and the spark in an atmosphere of nitrogen as sources. In the latter case the electrodes were placed parallel to the slit so that the pole effect might be obtained. It is w [illegible] tance is added to the circuit the radiations representi [illegible] ectra are confined more and more to the region of [illegible] es and finally disappear. The source of energy used [illegible] g a maximum of 30,000 volts with a condenser of small [illegible] the secondary. Schumann plates were used entirely and the exposures ranged from ten minutes to three hours, depending on the region photographed and the kind of source used. Two small pieces of cerium metal which were of a rather high degree of purity were kindly supplied by Dr. Stover of the Chemistry Department of this university, and were used as electrodes.

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Contribution from the Department of Physics, University of Alberta, Edmonton, Canada with financial assistance from the National Research Council of Canada.

[2] *Professor of Physics, University of Alberta.*

The spectrum is very rich in lines, as might be expected of an element in the position that cerium occupies in the atomic table, and it would be next to impossible to make any analysis without some means of separating the lines into the various stages of ionization.

Theoretical Analysis

After the spectrum had been photographed as stated above, the doublet suggested by Gibbs and White was examined carefully to make sure the lines really belong to Ce IV. This was clearly confirmed and the interval 4707 cm.$^{-1}$ was used throughout from λ2500 Å down to the limit of the spectrum photographed. This resulted in several pairs of lines, some of which seemed undoubtedly to be Ce IV lines. In particular the following three strong lines were outstanding on the plates of the vacuum spark:

1372.72 (75)	72,848.0
1332.16 (75)	75,066.0
1289.41 (50)	77,554.8

Fortunately, there are scarcely any other lines of comparable intensity in the neighborhood and certainly none of equal intensity. These three lines are clearly the 5D−6P multiplet. The relative intensity of the lines is characteristic of this multiplet in many similar spectra. The discovery of this multiplet was taken as strong confirmation of the reality of the 6S−6P doublet, and accordingly a fuller analysis of the spectrum was attempted on this basis.

TABLE I

THE SPECTRUM OF CE IV

Assignment	λ I.A.	Int.	Wave number	Interval	Configuration	Term	Term value
$6S_1-6P_2$	2456.86	45	40,690.1	4706 2	$5p^65d$	$^2D_2$	0 0
$6S_1-6P_1$	2778.20	90	35,983.9			$^2D_3$	2488.8
					$5p^66s$	$^2S_1$	36,864.4
$6P_2-6D_3$	2063.13	10	48,454.5	598.8			
$6P_2-6D_2$	2037.95	18	49,053.3	4707.3		$^2P_1$	72,848.0
$6P_1-6D_2$	1881.05	18	53,161.8		$5p^66p$	$^2P_2$	77,554.8
$6P_2-7S_1$	1779.03	20	56,210.4	4706.5	$5p^66d$	$^2D_2$	126,009.6
$6P_1-7S_1$	1641.58	15	60,916.9			$^2D_3$	126,608.1
$5D_2-6P_1$	1372.72	75	72,848.0	4706.8	$5p^67s$	$^2S_1$	133,765 0
$5D_3-6P_2$	1332.16	75	75,066.0	2488.8			
$5D_2-6P_2$	1289.41	50	77,554.8				
					$5p^68s$	$^2S_1$	182,895
$6P_2-8S_1$	949.30	3	105,341	4706			
$6P_1-8S_1$	908.70	1	110,047				
					$5p^67d$	$^2D_2$	183,996
$6P_2-7D_2$	939.49	1	106,441	223		$^2D_3$	184,219
$6P_2-7D_3$	937.52	3	106,664	4706			
$6P_1-7D_2$	899.71	3	111,147				

Table I shows the classified lines of Ce IV together with the wave numbers and intervals. The last column shows the term values measured upward from the deepest term $5D_2$ which has been given zero value. The values of the inner quantum number j have been increased by ½ to facilitate the printing of the report. The intensities are taken from plates of the vacuum spark spectrum. The confirmation of these assignments, aside from the question of equal intervals, is sought in the regular doublet law and the Moseley law. The results of the application of the regular doublet law, which has to do with the relation of intervals throughout an isoelectronic sequence of ions, are given in Table II. Cs I (2), Ba II(7) and La III(8), together with Ce IV, form such a sequence in which the spectrum arises from a single valence electron, a so-called stripped atom sequence in which each structure corresponds to a simple doublet spectrum. The table shows the screening constants s for the intervals $\Delta\nu$ for the 5D, 6P and 6D terms. It is evident from the table that the screening constants decrease in a normal fashion which one is led to expect from many other similar sequences.

TABLE II

THE REGULAR DOUBLET LAW

	$\Delta\nu$	Z	$\left(\frac{\Delta\nu}{K}\right)^{\frac{1}{4}}$	s
		$(5D_2-5D_3)$		
Cs I	98	55	10.60	44.40
Ba II	801	56	17.92	38.08
La III	1603	57	21.31	35.69
Ce IV	2489	58	23.79	34.21
		$(6P_1-6P_2)$		
Cs I	554	55	14.23	40.77
Ba II	1691	56	18.81	37.19
La III	3096	57	21.88	35.12
Ce IV	4707	58	24.30	33.70
		$(6D_2-6D_3)$		
Cs I	43	55	9.89	45.11
Ba II	205	56	14.61	41.39
La III	434	57	17.62	39.38
Ce IV	599	58	19.10	38.90

TABLE III

THE MOSELEY LAW VALUES OF $\sqrt{\frac{\nu}{R}}$ AND DIFFERENCES

	Cs I	Δ	Ba II	Δ	La III	Δ	Ce IV
$5D_3$	0.391	0.436	0.827	0.380	1.207	0.353	1.560
$6S_1$	0.535	0.322	0.857	0.304	1.161	0.295	1.456
$6P_2$	0.423	0.308	0.731	0.299	1.030	0.293	1.323
$6D_3$	0.283	0.278	0.561	0.286	0.847	0.294	1.141
$7S_1$	0.343	0.248	0.591	0.249	0.850	0.262	1.112
$8S_1$	0.254	0.200	0.454	0.207	0.661	0.227	0.888

In Table III the Moseley law has been applied to the corresponding term values throughout the same sequence. The differences are seen to be about as regular as those for the preceding row of similar structures (5) in the atomic table.

The few F terms in this sequence which are known appear highly irregular. In Cs I the 4F terms are unresolved because the combination with 5D falls in the infra-red, and the 5F terms are inverted and very narrow. In Ba II none of the three known F terms are inverted but all have virtually the same separation of about 225 cm^{-1}. In La III no F terms were discovered and it was suggested that the 5D−4F combination in this spectrum might lie in the infra-red, but an investigation as far as λ10,500 Å failed to reveal the lines (8). The author, who had been working independently on La III, found this combination in the ultraviolet:

$5D_2-4F_3$	1081.61(15)	92,454.7	
			1603.4
$5D_3-4F_4$	1099.73(15)	90,931.4	
			80.1
$5D_3-4F_3$	1100.70(7)	90,851.3	

These lines are isolated and outstanding on the vacuum spark plates and there seems no doubt of their correctness.

It does not seem possible to locate the corresponding 5D−4F multiplet in Ce IV without ambiguity on the author's vacuum spark plates. It would be expected about 650 Å but while there are several prominent lines near this value it may be that the satellite is missing. This is unfortunate because of the interest in deciding whether the first electron bound to the stripped atom is $5d$ or $4f$. It seems at present that there must be something erroneous about the F terms of Ba II and these should be carefully investigated again.

The 6P−8S doublet in La III has also been located:

$6P_2-8S_1$	1399.01	(2)	71,480
$6P_1-8S_1$	1462.26	(5)	68,387

The ionization potential can be found approximately for the Ce IV ion. There are three S terms available and at least two D terms. The 6P−7D multiplet is not very certain and the $7d\ ^2D$ term is therefore probably doubtful. Simply by using a Rydberg table, and having in mind the sequence of term values in Table III, the value of the deepest term is approximately 269,500 cm.$^{-1}$ which corresponds to an ionization potential of 33.3 volts compared with 33.8 volts for Zr IV (5). A similar close agreement is found for Yt III(6) and La III(8) both of which give a value close to 20 volts. It should be stated that the term values for La III on which Table III is based are about 4% greater than those given by Russell and Meggers, in order to make the run of values for the Moseley law as uniform as possible.

Acknowledgment

The author wishes to thank Dr. Stover for the cerium metal.

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MEASUREMENT OF SMALL CAPACITIES IN TERMS OF MUTUAL INDUCTANCE AND RESISTANCE[1]

By W. H. Watson[2]

Abstract

Campbell's a-c. bridge for the measurement of self-inductance in terms of mutual inductance can be modified so as to measure small capacities (1–1000 $\mu\mu f.$). The arrangement described is sensitive to within 0.01 $\mu\mu f.$ Small condensers can be measured to within 1% with ease. Residual errors are discussed.

The method described here for measuring small capacities suggested itself from an observation in the course of an exercise with Campbell's bridge for the measurement of self-inductance in terms of mutual inductance (1, p. 298). It was found that when a resistance of a few thousand ohms was joined between the source and the secondary of the mutual inductance, M, the value of M for balance instead of being zero as expected, turned out to be about 0.1 mh. Inspection of the disposition of the circuit made it reasonable to suppose that this disturbance of the normal condition of balance was due to capacity in the position indicated by C in Fig. 1. This hypothesis was soon justified by calculation and by subsequent measurements in which a known capacity was used, and the apparatus arranged so as to reduce stray capacity. It was recognized that this circuit offers a sensitive means of measuring small capacities which it is convenient to use whenever Campbell's variable standard and balancing inductance are available.

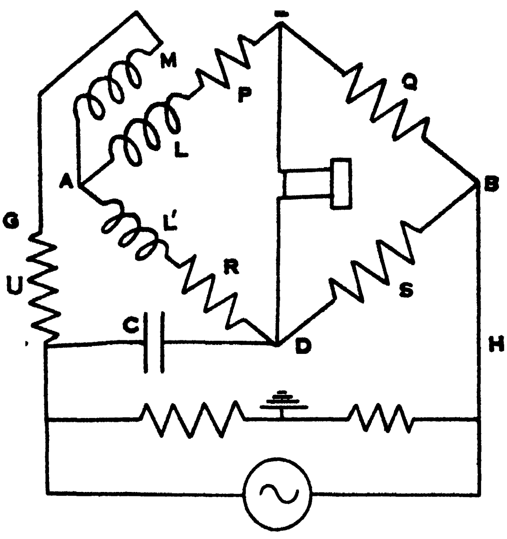

Fig. 1.

If l_1 denotes the effective inductance between F and A, and U the total resistance, and the other quantities are as indicated in the figure, then it can readily be established by a double transformation of the network (1, p. 47) that the following are the conditions for no current through the detector when the source supplies an e.m.f. of angular velocity p:

$$L'\frac{Q}{S} - L + M\left(\frac{Q}{S} + l_1\right) = C\{U(P+R) + RP - p^2[(L+L')l_1 + LL' - 2ML' - M^2]\} \qquad (1)$$

and

$$\frac{QR}{S} = P - p^2C\{(U+R)(L-M) + P(l_1+L') + U(L'+M) + R(l_1-M)\} \qquad (2)$$

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Contribution from the Department of Physics, McGill University, Montreal, Quebec, Canada.

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The conditions of balance are dependent on the a-c. frequency employed, but if C is small, U has to be made large for sensitivity, so that, when L' is the proper balancing coil for the primary of M, Condition (1) becomes approximately:

$$M\left(\frac{Q}{S}+1\right) = CU(P+R) \tag{3}$$

and in any case the frequency need not be known very accurately if a more precise measurement is required.

The method of measurement is to make a preliminary test of Campbell's bridge with U and C absent. M should be equal to zero or very nearly so. U is then introduced and the bridge balanced with the condenser C out of circuit, but with the leads to it in position. Only a very small change in M and P should be required when this arrangement is made; if this is not the case, there is probably stray capacity between U and some part of the bridge. The condenser is next connected and M and P adjusted for balance; for a small capacity, the change in P will not be great but will depend on the frequency, while the change in M can be made to have any desirable value by the proper choice of Q/S and U. With an equal ratio bridge the well known advantages with respect to residuals in the ratio arms are secured, but as the balancing coil L' is usually supplied for $Q/S = 9$ it is convenient to use this, and it is possible to measure easily, within 1%, capacities of a few micromicrofarads. A further advantage of the ratio 9 : 1 is that it makes U larger and the bridge therefore more sensitive for the measurement of C, while, as a less important consequence, the large value of U renders the approximate formula (Equation (3)) applicable for routine work.

Provided that a suitable source and detector are available, there is no difficulty in establishing an accurate balance of the bridge which can be made sensitive to within 0.01 $\mu\mu$f., but it is obvious that such a bridge may also be seriously affected by residuals in the resistance boxes and other apparatus employed, and in the actual arrangement of the apparatus and connections. By far the most important sources of error due to residuals arise from neglect of the residual capacity of the resistance U, and from the presence of appreciable capacity between G and D. The latter can be kept small, if care is taken in setting up the bridge, its presence being clearly demonstrated if P has to be altered very much when U is introduced into the circuit. It can be easily shown that capacity between G and D produces changes in the effective values of U and C which, however, are not serious because they leave the product CU unaltered. In addition, however, it may make a large negative contribution to l_1 and this also is the effect of the self-capacity of U. For, if U is shunted by a small capacity k, the impedance operator is $U - jpkU^2$ (kU being small); there is therefore a contribution $-kU^2$ to l_1. Provided that P is not small—a condition which is desirable on other grounds—the effect of l_1 in Equation (1) will generally be negligible, if 1% accuracy is all that is required. On the other hand, the effect of l_1 in Equation (2) will always be important, and may lead to a decrease in P when C is introduced.

Impurity in the mutual inductance will enter as a correction to P which becomes of less importance the greater P is. P cannot be made greater than about 1000 ohms without introducing error due to its self-capacity. If the condenser is an impure one with effective series resistance ρ, the term $QR\rho C/S$ enters Equation (1) and is obviously quite negligible. Residual inductance in the ratio arms is of importance only in the second condition of balance (Equation (2)).

When it is required to measure a condenser of capacity less than 1000 $\mu\mu$f. by this method, the suitable values to be given to P, R, Q, S are fairly well determined by the above considerations. The writer has, however, investigated the effects of varying p, U, R and Q, and the influence of a small capacity shunting Q or U, and found that, provided that the apparatus is well arranged so as to reduce capacity between the arms of the network, consistent measurements of C can be obtained, even if these variables are not kept within narrow limits.

Some sample measurements are given in Table I. A valve oscillator supplying a.c. of 806.3 cycles per second was coupled by a step-up transformer to an earthing device (1, p. 368) and from that to the bridge by means of shielded cable. As detector, telephones were used with an amplifier giving a 1000 : 1 gain, coupled through a shielded transformer to the bridge. Two condensers were measured; one was a General Radio Type 222 precision condenser, with the maker's calibration available, the other was a variable cylindrical condenser whose capacity was calculated from geometrical data. As a matter of interest, the grid-plate capacity of a triode 201A was measured and found to be 10.1 $\mu\mu$f.

The results given in Table I indicate how well the mutual inductance can be set and the satisfactory agreement between the measured values of C and the data of the maker. Neglect of PR and l_1 in Equation (1) leave the values of C obtained by means of Equation (3) not more than 4 parts in error per 1000. There is no reason why one should not attempt to evaluate these corrections if higher accuracy is required, but, of course, the amount of work involved is very much greater. In the fifth column of Table I the quantity $(SP - RQ)/SC$ is given; according to Equation (2) it should be a constant and if U had no self-capacity, would yield the value of $U(L + L')p^2$, and hence $L + L'$. The result is 19.2 mh., which is to be compared with the known value 24.8 mh. If this large difference were due entirely to the residual capacity of U, the capacity in question would have to be 56 $\mu\mu$f. or the effective inductance l_1 would have to be -0.56 h. In order to check this, U was connected to a balanced Schering condenser bridge (1, p. 242) in parallel with the arm S of 2000 ohms. The capacity shunting S was found to be 56.2 $\mu\mu$f. This is an excellent agreement, for the other residuals already discussed could account only for a small part of the difference 24.8 − 19.2 mh. referred to.

In the above-mentioned experiments the error introduced in the value of C due to neglect of the effect of the residual capacity of U on its effective resistance $U(1 + p^2k^2U^2)^{-1}$ is only 0.06%. One should not however overlook the fact that a serious error may arise from this source if p or k happens to be larger. Attention has been drawn by Jones and Josephs (2) to the errors in high resistances caused in this way. It is important to notice that in other bridges for measuring small capacities and depending on the use of a high resistance, this residual must be kept in mind, and it is perhaps not out of place to mention that in a discussion of residuals in Anderson's bridge, Hague (1, p. 261) omits this effect in r.

TABLE I

(a) G.R. Type 222 condenser

C (maker), $\mu\mu f$.	M, μh.	P, ohms	C, Eqn. (3), $\mu\mu f$.	$\frac{SP - RQ}{SC} \times 10^{-10}$
Out of circuit	3	921.1	0.3	—
48	496	923.4	48.3	4.79
98	1003	925.9	97.7	4.90
217	2242	931.8	216.7	4.93
340	3543	937.9	340.6	4.94
466	4881	944.1	466.4	4.89
593	6247	950.4	593.3	4.91
782	8317	959.4	783.3	4.90
1028	11,063	971.9	1029	4.94

(b) Cylindrical condenser

Condenser scale reading, cm.	M, μh.	P, ohms	C, $\mu\mu f$.	Differences, $\mu\mu f$.	$\frac{\mu\mu f.}{\text{cm.}}$
3.00	172	921.2	16.77		
8.00	265	921.6	25.87	9.10	1.82
10.00	302.5	921.8	29.54	12.77	1.82
13.00	359	922.1	35.04	18.27	1.83

Frequency = 806.3 cycles/sec. Q/S = 900/100; U = 100,000 ohms. The maximum resistance and self-inductance of the secondary of M are 10 ohms and 9 mh. respectively. R = 102.4 ohms.

The calculated value of the capacity per cm. of the coaxial cylinder was 1.85 μμf./cm. (first approximation).

It was suggested to the writer by Dr. H. G. I. Watson that the places of U and C in the network might be changed, with advantage, to the following:— U between B and H and C between D and H. With this arrangement which is practically the conjugate network to Anderson's bridge, the conditions of balance are

$$-M\left(\frac{Q}{S} + 1\right) = C\left\{RU\left(\frac{Q}{S}+1\right) + RQ - p^2(L'+M)l_1\frac{Q}{S}\right\} \tag{4}$$

and

$$= \frac{QR}{S} - p^2C\left\{l_1\left(\frac{Q}{S}+1\right)R + (L'+M)\left[\left(\frac{Q}{S}+1\right)U + Q\right]\right\}. \tag{5}$$

If l_1 were zero, then Condition (4) would be independent of the frequency, but as l_1 is quite large the arrangement can be quite inaccurate for measuring any but the smallest condensers unless an equal ratio bridge is used. Even when $Q/S = 1$, the error introduced by neglect of l_1 in determining C may be larger than with U and C on the other side of the bridge, on account of the fact that l_1 is multiplied by M*. This objection would also apply in a slightly modified form to the use of the Campbell-Heaviside equal ratio bridge. These conclusions are supported by experiment.

Acknowledgment

The writer is indebted to Dr. H. G. I. Watson for helpful discussion and for assistance in some of the measurements.

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*Provided that the effective self-inductance due to the residual capacity of U were balanced out by the inclusion of an equal self-inductance in series with U, this arrangement would be far more convenient, because P, which is adjusted for balance, does not appear in Equation ([illegible]), and then if $R = 100$ ohms, $U = 10^6$ ohms, the mutual inductance would give C directly as $M/10$ μμf., M being in μh.

ANOMALOUS DISPERSION OF SOUND IN SOLID CYLINDRICAL RODS[1]

By R. Ruedy[2]

Abstract

The deviation of the overtones from whole multiples of the fundamental note when pure longitudinal waves are set up in a cylindrical rod, one to a few centimetres in thickness, is accounted for to within less than 1% by the drop in the velocity of propagation of longitudinal waves with increasing frequency due to radial motion in the rod. The radial component present in vibrating solid or hollow cylinders determines a second solution of the velocity equation which starts near the resonance frequency of the radial vibration. Although radial motion can take place free from longitudinal components, so that no mutual coupling need exist between the two types of vibration, the equation for thin rods can within certain frequency ranges be reduced to the frequency relations valid for coupled systems.

Introduction

The velocity of propagation, c, of longitudinal waves of sound of frequency f, in a solid cylindrical rod of radius a, is given by the formula.

$$1 - \frac{c^2}{c_0^2}\frac{m+1}{m} = \frac{1 - \dfrac{kaJ_0(ka)}{J_1(ka)}}{1 - \dfrac{\dfrac{c^2}{c_0^2}\dfrac{(m+1)}{m} - 1}{\dfrac{c^2}{c_0^2}\dfrac{(m-2)(m+1)}{(m-1)m} - 1}\;\dfrac{h_1aJ_0(h_1a)}{J_1(h_1a)}},$$

where

m = the reciprocal of Poisson's ratio μ

c_o = velocity of sound at low frequencies

$$k = \frac{2\pi}{c/c_0}\,\frac{f}{c_0}\sqrt{\frac{2(m+1)}{m}\frac{c^2}{c_0^2} - 1}$$

$$h_1 = \frac{2\pi}{c/c_0}\,\frac{f}{c_0}\sqrt{\frac{(m-2)(m+1)}{(m-1)m}\frac{c^2}{c_0^2} - 1}$$

As long as c^2/c_o^2 is smaller than $(m - 1)m/(m + 1)(m - 2)$, h_1 is an imaginary quantity ih.

With the usual values of m, the velocity decreases first slowly from c_o to about $0.9c_o$, reached near the frequency $c_o/4a$, and then drops more rapidly to about $0.6\ c_o$ near the frequency $0.4\ c_o/a$, where an apparent discontinuity occurs. How well the theory agrees with the measurements is shown in Table I for

TABLE I

Observed and computed velocities of sound in cylindrical rods of nickel

Frequency, kc. per sec.	Velocity, c/c_o	f/c_o, observed	f/c_o, calcd.
188.7	0.9526	0.381	0.381
226.9	0.9164	0.458	0.459
242.8	0.8913	0.490	0.492
256.5	0.8631	0.518	0.525
270.1	0.8391	0.545	0.547

Length of rod, 100 mm.; diameter, 10 mm.; $m = 3.25$, $c_o = 4952$ m. per sec.

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[1] *Manuscript received May 17, 1935.*
Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

[2] *Research Investigator, National Research Laboratories, Ottawa.*

nickel rods and in Figs. 1 and 2 for thin steel, aluminium and copper rods through which sound, in some cases, of nearly one million cycles per second, was sent (3, 5). Since the velocity depends merely on the product *fa*, and not on *f* and *a* separately, the results have been calculated on the basis of a diameter of 1 cm., which is the thickness of the nickel rod. The normal values of Poisson's ratio for nickel (0.31) and steel (0.29) have been adopted, with no attempt to improve the results by adjusting this ratio which differs slightly from rod to rod, depending on the history of the sample. The ratios adopted for aluminium and copper are lower than normal, 0.31 in place of 0.33, but the rods are vibrating in air, and the damping thus introduced tends to lower the natural frequency of thin rods.

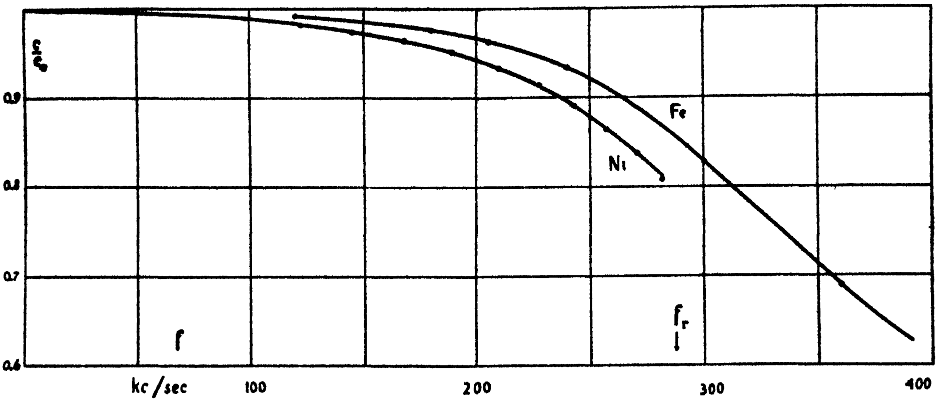

FIG. 1. *Velocity of sound as a function of the frequency, f, for cylindrical rods of nickel and steel, 1 cm. thick. The curves represent theoretical values, the dots observed ratio of the velocity, c, to the velocity c_0, at low frequencies (3).*

According to the theory, in materials having the same number *m*, the velocity c/c_0 varies in the same way, providing that it be plotted as a function of f/c_0. Fig. 2 illustrates this point for aluminium and copper; the data obtained for both metals fall upon the same curve.

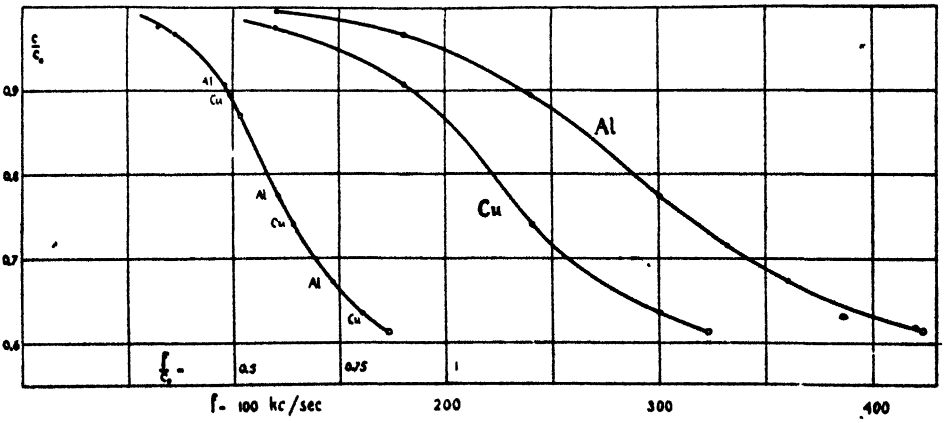

FIG. 2. *Velocity of sound, as a function of the frequency, for cylindrical rods of copper and aluminium, 1 cm. thick (3). The circles represent computed, the black dots observed, values. At the left the results are plotted as a function of f/c_0, using 0.32 as Poisson's ratio; lower values of this ratio shift the curve slightly to the right.*

The measured velocities refer to standing rather than progressive waves. Since the rigorous solution for standing waves does not result in a purely periodic function of the radial and longitudinal motion taken separately, a correction would have to be applied to the observed velocities. In the case of the rods in question, all less than one centimetre thick, the end effects are negligible and the correction may be disregarded. For thicker rods standing waves can no longer be represented as the result of two longitudinal waves progressing in opposite directions.

For velocities smaller than c_0, the displacements u, in the direction of the radius, and w, in the direction of the axis of the rod, are for any position, z, along the axis given by

$$u = \gamma J_1(ka)\left(\frac{J_1(kr)}{J_1(ka)} - \left(1 - \frac{c^2}{c_0^2}\,\frac{m+1}{m}\right)\frac{J_1(ihr)}{J_1(iha)}\right)\epsilon^{i(\gamma z + pt)}$$

$$w = \left(ka\frac{J_0(kr)}{J_1(ka)} + \frac{\dfrac{c^2}{c_0^2}\,\dfrac{m+1}{m} - 1}{\dfrac{c^2}{c_0^2}\,\dfrac{(m-2)(m+1)}{(m-1)m} - 1}\,\frac{haJ_0(ihr)}{iJ_1(iha)}\right)\frac{iJ_1(ka)}{a}\,\epsilon^{i(\gamma z + pt)}$$

or, at the surface of the rod, by

$$u = 2\pi\frac{f}{c}\,\frac{m+1}{m}\,\frac{c^2}{c_0^2}\,J_1(ka)\,\epsilon^{i(\gamma z + pt)}$$

$$w = \left(1 + \frac{\dfrac{c^2}{c_0^2}\,\dfrac{(m+1)}{m} - 1}{\dfrac{c^2}{c_0^2}\,\dfrac{(m-2)(m+1)}{(m-1)m} - 1}\,\frac{haJ_0(iha)}{iJ_1(iha)} - \left(1 - ka\frac{J_0(ka)}{J_1(ka)}\right)\right)i\,\frac{J_1(ka)}{a}\,\epsilon^{i(\gamma z + pt)}$$

apart from a constant factor C, which is given by the initial conditions and which may be made equal to unity by a suitable choice of the units in which u and w are measured. When applying the formulas, the function

$$\epsilon^{i(\gamma z + pt)} = \cos(\gamma z + pt) + i\sin(\gamma z + pt)$$

is split up so as to render u and w real, whether $J_1(kr)$ be real or imaginary. However, as k approaches zero, the displacements at the surface ($r = a$) vanish; the rod appears motionless, and the common methods of measuring the velocity of sound fail in this range. For solutions with still smaller values of c/c_0, and imaginary values of k, the displacements u and w would grow beyond any limit as the frequency is increased, so that it seems legitimate to reject solutions with imaginary values of k on the ground that they lead to a contradiction with the assumptions on which the velocity formula is based. Attempts to study the propagation of sound waves in this region have thus far met with failure despite the use of powerful sources of vibration (5).

Velocities at Higher Frequencies and Anomalous Dispersion

Although it seems difficult, on account of the small amplitude, to follow the propagation of frequencies higher than about 0.45 c_0/a through solid rods, the curve representing c/c_0 as a function of f/c_0 resembles, near this point, the curves representing anomalous dispersion, so that it seems worth while to ascertain the value of f/c_0 for very high values of c/c_0. In this case the equation giving the velocity of sound becomes

$$-\frac{c^2}{c_0^2}\frac{m+1}{m} = \frac{1 - la\dfrac{J_0(la)}{J_1(la)}}{1 - \dfrac{m-1}{m-2}\,ga\dfrac{J_0(ga)}{J_1(ga)}} \quad \text{for } \frac{c}{c_0} \gg 1 ,$$

where now, with $la < 1.841$ and $\gamma = 0$,

$$l = 2\pi\frac{f}{c_0}\sqrt{\frac{2(m+1)}{m}} \qquad g = 2\pi\frac{f}{c_0}\sqrt{\frac{(m-2)(m+1)}{(m-1)m}}$$

$$3 > \frac{l}{g} = \sqrt{\frac{2(m-1)}{m-2}} > 1$$

The right-hand side of the equation becomes very large when

$$\frac{m-2}{m-1} = ga\frac{J_0(ga)}{J_1(ga)} .$$

This relation, however, represents but the resonance condition for pure radial waves along the rod. A kind of anomalous dispersion is of course to be expected in solid, as well as in hollow, rods. The values of ga satisfying the equation are given in Table II.

TABLE II

SOLUTIONS OF THE EQUATION $(m-2)J_1(ga) = (m-1)gaJ_2(ga)$

m	$(ga)_1$	$(ga)_2$	$(ga)_3$	l/g	μ	Material
2.22	2.325	5.483			0.45	Lead
2.50	2.254	5.451		2.45	0.40	Gold
3.00	2.166	5.428	8.595	2.00	0.33	Aluminium
3.33	2.126	5.414		1.87	0.30	Nickel
4.00	2.069	5.396	8.576	1.73	0.25	Glass

The frequency, f_r, at which the velocity tends to infinity, is obtained from

$$\frac{f_r}{c_0} = \frac{(ga)}{2\pi a}\sqrt{\frac{m(m-1)}{(m+1)(m-2)}} .$$

For $m = 3.25$ the value of f_r/c_0 is 0.76, so that the radial resonance frequency of a long rod is higher than the radial resonance frequency of a thin circular disc (1). However, in so far as it involves extremely high velocities of propagation, the computed resonance frequency is probably higher than the actual value. Oscillations which appear to form the radial resonance system have been observed at 287.5 kc. per sec. for a nickel rod, that is, when f/c_0 is equal to about 0.58, instead of at 330 kc. per sec.

Close to the radial resonance frequency, f_r, small changes in f/c_0 bring the velocity back to normal values, so that h and k must again be used in place of g and l. Near $c/c_0 = 1$ the velocity drops more slowly as the frequency is further increased, the ratio c/c_0 reaching the value $(m/(m+1))^{\frac{1}{2}}$ for

$ka = 5.33$, when $m = 3.5$ and f/c_0 is equal to about 1.5. The condition for a second region of radial resonance (near $f/c_0 = 2$ for $m = 3.25$) is then approached; but for these high frequencies the size of the grains making up the metal must make itself felt. In the descending branch of the curve the velocity remains greater than the value c for which $c^2/c_0^2 = m/2(m+1)$ and k is equal to zero since only one solution f exists for this point (4).

Resonance Frequencies in Rods and Frequencies in Coupled Systems

For the use of rods as frequency standards, a simple formula is desirable. Since in the range that is of practical interest, ha and ka for a rod 1 cm. in diameter are smaller than about four and as long as the diameter is small compared with the wave-length, the Bessel functions occurring in the velocity equation may be replaced by the first few terms of their development in series:

$$J_0(ha) = 1 - \frac{h^2a^2}{4} + \frac{h^4a^4}{64} - \frac{h^6a^6}{2304} + \ldots$$

$$J_1(ha) = \frac{ha}{2}\left(1 - \frac{h^2a^2}{8} + \frac{h^4a^4}{192} - \frac{h^6a^6}{9216} + \ldots\right).$$

Moreover, putting

$$e^2 = 1 - \frac{c^2}{c_0^2}\,\frac{m+1}{m} = 1 - \frac{c^2}{c_0^2}(1+\mu)$$

$$h = 2\pi\frac{f}{c}H,$$

and retaining terms in $(ha)^4$ and $(ka)^4$ only, the equation becomes, outside the region of radial resonance,

$$\frac{a^4}{192}\left((h^2-k^2)^2\left(1+e^2+\frac{2e^4}{H^2}\right)+4k^4+7h^2k^2+h^2k^2\left(\frac{8e^4}{H^2}+e^2-7\right)\right)$$
$$-\frac{a^2}{8}\left((h^2-k^2)\left(1+e^2+\frac{2e^4}{H^2}\right)-2k^2+2e^4\frac{h^2}{H^2}\right)+\left(1+e^2+\frac{2e^4}{H^2}\right)=0,$$

where

$$1+e^2+\frac{2e^4}{H^2}=\frac{c^2}{J'^2c_0^2}\left(1-\frac{c^2}{c_0^2}\right)\frac{(m+1)^2}{m(m-1)}.$$

If the last term only is considered, the solution leads to a constant value $c = c_0$. The last two terms give

$$\frac{c^4}{c_0^4}+\frac{c^2}{c_0^2}\,\frac{\dfrac{8c_0^2}{a^2p^2}-7+\dfrac{2\mu^2}{1-\mu}}{(1+\mu)\left(4(1-\mu)+\dfrac{1-2\mu}{1-\mu}\right)-\dfrac{8c_0^2}{a^2p^2}}$$
$$+\frac{2}{(1+\mu)\left(4(1-\mu)+\dfrac{1-2\mu}{1-\mu}\right)-\dfrac{8c_0^2}{a^2p^2}}=0.$$

When the assumption is made that $c^2/c_0^2 = 1 + \eta a^2$, and $8c_0^2/a^2p^2$ is replaced by $8c_0^2/a^2c^2\gamma^2$, the well-known formula

$$\frac{c}{c_0} = 1 - \frac{\mu^2a^2\gamma^2}{4}$$

is obtained.

Considering that for standing waves, n being a whole number

$$p = 2\pi f = n\pi \frac{c}{L},$$

with sufficient accuracy for thin rods of length L,

$$\frac{c^4}{c_0^4} - \frac{c^2}{c_0^2} \frac{\frac{8L^2}{n^2\pi^2a^2} + 7 - \frac{2\mu^2}{1-\mu}}{(1+\mu)\left(5 - 4\mu - \frac{\mu}{1-\mu}\right)} + \frac{\frac{8L^2}{n^2\pi^2a^2} + 2}{(1+\mu)\left(5 - 4\mu - \frac{\mu}{1-\mu}\right)} = 0,$$

or approximately

$$\frac{c^4}{c_0^4} - \frac{c^2}{c_0^2} \frac{\frac{4L^2}{n^2\pi^2a^2} + \frac{7}{2} - \frac{\mu^2}{1-\mu}}{\frac{5}{2}(1-\mu^2)} + \frac{\frac{4L^2}{n^2\pi^2a^2} + 1}{\frac{5}{2}(1-\mu^2)} = 0.$$

On the other hand, when the rod is considered as a system in which the longitudinal vibrations are mechanically coupled with the radial vibrations of thin sections, for which the resonance frequency is given by

$$f_{0r} = \frac{\zeta c_0}{2\pi a}\sqrt{1-\mu^2},$$

where ζ is the solution of the equation for radial oscillations of thin discs,

$$\zeta \frac{J_0(\zeta)}{J_1(\zeta)} = 1 - \mu,$$

and is closely equal to 2, then (1)

$$\frac{c^4}{c_0^4} - \frac{c^2}{c_0^2} \frac{\frac{\zeta^2L^2}{n^2\pi^2a^2} + (1-\mu^2)}{\frac{1-2\mu}{(1-\mu)^2}(1-\mu^2)^{\frac{3}{2}}} + \frac{\frac{\zeta^2L^2}{n^2\pi^2a^2}}{\frac{1-2\mu}{(1-\mu)^2}(1-\mu^2)^{\frac{3}{2}}} = 0.$$

There is a certain resemblance between the two equations, which explains why over a certain range the theory of coupled vibrations is capable of representing the results with great accuracy, though it fails completely as a general expression. The formula based on the velocity equation, on the other hand, is valid whenever longitudinal oscillations exist alone in thin rods, while flexural vibrations, or in the case of thicker rods, vibrations characteristic of plates, are absent. Both formulas give two branches for the resonance curve; in the case of coupled vibrations the two branches are separated by a silent zone; in the case of the solid rod they overlap, in qualitative agreement with the observations (1).

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THE THERMAL CONDUCTIVITY OF SUNDRY MATERIALS[1]

By C. D. Niven[2]

Abstract

The results of measurements on the thermal conductivity of acetylene black, rock wool, sphagnum moss, dried asbestos-water paste and other insulators are given.

The descriptions of the samples of insulating materials whose thermal conductivity is reported in this paper are those which the manufacturers furnished.

The results on sphagnum peat moss are of so much commercial interest at the present time that some results of Dr. Finck's (1), taken from a Bureau of Standards publication, are quoted in Table I. These results were obtained with dried material and are therefore slightly lower than those reported in Table II. The general agreement, however, is remarkably good.

TABLE I

Thermal conductivity of sphagnum moss, as determined by Finck

Moisture,	Density, lb./cu.ft.	Mean temp., °F.	Conductivity, B.t.u./hr./sq. ft./°F./in.
Negligible	3.0	90	0.251
Negligible	3.4	90	0.256
Negligible	4.5	90	0.248
Negligible	5.4	90	0.237
Negligible	9.9	90	0.278
Negligible	16.7	90	0.339

Note:— *Quoted from Reference (1), p. 976.*

There is an indication that the thermal conductivity of sphagnum peat moss increases linearly with the density and that the rate of increase is somewhat similar to that of wood fibre. This result is of course to be expected since compressing would mainly have the effect of squeezing the air out of the sample. Sphagnum peat moss is clearly a good insulator but its exceedingly hygroscopic nature should not be forgotten by those who would stress the economy which can be effected by its use.

The samples of rock wool, with one exception, were supplied by Mr. M. F. Goudge and are fully described by him in a memorandum (2) of the Mines Branch. The results indicate that the quality of the rock wool rather than the density of packing is the important factor affecting the thermal conductivity.

The samples of asbestos were prepared by Mr. D. Wolochow, chemist in charge of the asbestos research work undertaken by the Division of Chemistry of the National Research Council. The results of the experiments indicate that both the length of the fibre and the quantity of water used in making

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[1] *Manuscript received April 18, 1935.*
Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

[2] *Physicist, National Research Laboratories, Ottawa.*

TABLE II

DESCRIPTION AND THERMAL CONDUCTIVITY OF SAMPLES

Material	Description	Thickness at which sample was measured, in.	Moisture, %	Density, lb./cu. ft.	Mean temperature, °F.	Conductivity, B.t.u./hr./sq. ft./°F./in.
Acetylene black	50% compressed	1.117	0.7	5.5	53	0.268
	Uncompressed	1.090	1.5	2.2	55	0.220
Chopped straw	Treated for fire resistance	1.148	6.0	8.1	53	0.361
Corrugated board	Double, corrugations horizontal	0.335	—	11.8	53	0.366
Corrugated aircell insulating board	9/16 in., corrugations horizontal	0.722	—	8.05	54	0.353
	5/16 in., corrugations horizontal	0.354	—	7.6	52	0.338
Rock wool	Long fibre, moderately coarse	1.083	Negligible	3.0	53	0.271
	Granulated	1.099	Negligible	8.7	53	0.280
	Fine, almost free from shot	1.100	Negligible	7.9	54	0.230
	Fine, containing considerable shot	1.110	Negligible	10.3	55	0.248
	Pad containing a small amount of bonding material	0.700	Negligible	11.3	54	0.248
		1.099	Negligible	7.9	55	0.242
		1.240	Negligible	6.6	55	0.242
	Commercial	1.100	Negligible	6.1	55	0.247
Specially ground wood fibres	Calcium treated	1.090	8	5.5	56	0.317
		1.190	7	6.0	57	0.328
Sphagnum peat moss	Board	1.328	11.0	10.2	59	0.309
	Loose	1.106	11.0	3.9	58	0.264
	Loose, charred	1.192	7.6	16.2	57	0.382
	Fine ground, moist	1.083	25	3.9	58	0.256
	Rough, very moist	1.114	30(?)	2.3	56	0.362
	Shredded	1.104	9.6	3.5	56	0.258
	Loose	1.183	10	8.5	59	0.271
		1.110	10	9.8	63	0.289
		1.102	10	4.7	59	0.272
Asbestos–water paste moulded by hand and dried*	Short fibre; 120% mixing water	0.698	Negligible	56	633	1.80
	Short fibre; 100% mixing water	0.731	Negligible	60	611	1.98
	Short fibre; 80% mixing water	0.826	Negligible	64	638	2.19
	Very short fibre; 100% mixing water	0.916	Negligible	64	608	2.39
	Very short fibre; 75% mixing water	0.808	Negligible	68	613	2.11
	Very short fibre; 65% mixing water	0.849	Negligible	74	643	1.99
	Fine ground serpentine; 80% mixing water	0.855	Negligible	69	634	1.69

* *Short fibre refers to Quebec Standard Screen Test 0-0-4-12. Very short fibre refers to Quebec Standard Screen Test 0-0-1-15. The fine ground serpentine was 200 mesh material.*

the samples affect the thermal conductivity. As shown in Table II, these measurements were carried out at a temperature much higher than the temperatures at which the other measurements were made, since, of course, asbestos is essentially an insulator for use at temperatures higher than room temperature.

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A HYDROGEN DISCHARGE TUBE FOR ABSORPTION SPECTROSCOPY[1]

BY W. H. WATSON[2] AND D. G. HURST[3]

Abstract

An inexpensive, easily assembled tube of rugged construction is described. All parts exposed to the discharge are water cooled. The capillary with its water-cooling sheath is the only glass part, is a self-contained unit and is easy to make. The tube has been operated without trouble at over 2 kw. input at 1000 volts.

The tube was designed for use with a vacuum spectrograph, where mechanical soundness of construction and high light intensity are required. The problems confronting the designer of such a discharge tube are well known (1, 2, 3, 4, 6). It is necessary to cool the electrodes and the narrow tube* in which the discharge is constricted in order to obtain high current density. The cooling of the latter presents a serious problem in the H-type of tube in which the horizontal arm of the H has to join two large tubes carrying the electrodes, and the resulting system is necessarily mechanically weak. So long as one is restricted to the traditional practice of supporting all the parts of the discharge tube in a glass envelope, one requires glass-work which is fairly elaborate and expensive if account is taken of its strength and probable life.

It was with the object of eliminating unnecessary glass parts that the tube to be described was constructed, and as a tube of this type has been operated successfully in this laboratory the writers feel that it is useful to give the details of its construction.

The main innovation in tube construction is that the water-cooled capillary is a self-contained unit which may be made of glass or quartz as desired, and which is held in the water-cooled hollow electrodes at each end by means of rubber tubing not exposed to the discharge. The electrodes themselves are rigidly connected with each other by two ebonite strips, so that the capillary has no part in determining the relative position of the electrodes. Each electrode has a hole drilled along its axis, one for the axial emission of light through a fluorite window waxed into the electrode, the other for connection to a pressure-stabilizing reservoir and to the pump and hydrogen supply.

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[1] *Manuscript received July 10, 1935.*
Contribution from the Physical Laboratory, McGill University, Montreal, Quebec, Canada.

[2] *Assistant Professor of Physics, McGill University.*

[3] *Holder of a bursary under the National Research Council of Canada.*

**The narrow tube will be referred to hereinafter as the capillary although the internal diameter that used in this tube was 6.5 mm.*

The details of the construction of the tube are shown in Fig. 1. The electrodes, AA, shaded diagonally, are of aluminium alloy, heat treated for machining, and were turned from sections of a rod 3 in. in diameter. This metal was chosen on the basis of Lyman's remarks on the hydrogen spectrum (5, p. 89) and ease of working. The water jackets, BB, are of brass tubing and are screwed into place by means of brass collars soldered on one end of each. The joints are made watertight with a packing of graphite and cord. Fixed to the electrodes by screws are two square brass plates, CC, attached to which are the ebonite distance pieces indicated by the dotted lines in the figure.

Thus all the metal parts are fixed together and the glass capillary hangs on the rubber tubes DD, each of which slips on a separate aluminium tube, GG, making a sliding fit in the electrode. The reason for using this method rather than having the projection for the rubber tube a part of the electrode is twofold; both the boring of the electrode and the assembly of the lamp are facilitated. The wax joints are sufficiently distant from the ends of the capillary to remove them from exposure to the discharge; they are made with "pizein" wax. The rubber tube E takes up any expansion of the capillary and prevents a complete circuit of glass. It is sealed with tar. To ensure that the water reaches the ends of the capillary, deflectors, FF, of thin copper are used. The capillary can be silvered, if desired, to promote recombination of the hydrogen.

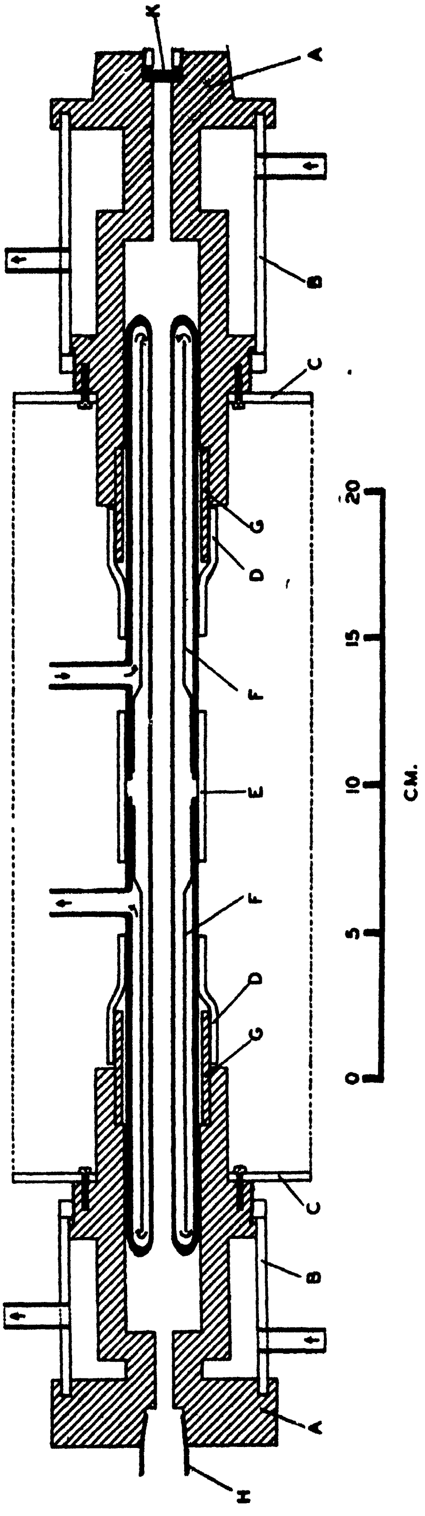

FIG. 1. *A hydrogen discharge tube for absorption spectroscopy.*

The connection to the pump and reservoir, etc., is a glass cone, H, fitting into the electrode and waxed in place. The electrodes are heated for waxing by passing steam into the water jackets.

In use this tube gives an intense spectrum which has been photographed with the Hilger E50 vacuum grating spectrograph. The exposures are 30 to 45 sec. with a slit width of 0.006 cm. and a measured power of 1.5 kw. So far, the power input actually dissipated in the tube at 1500 volts has not exceeded 2.2 kw., but as this order of exposure is satisfactory for the purpose in hand, greater power is not necessary. The writers are therefore ignorant of the breakdown limit of the tube. Nevertheless, experience with a forerunner of this apparatus makes them confident that much greater power can be handled safely.

In this design the writers have wittingly given up the freedom from sputtering inherent in the H type of tube, but feel that the advantages gained with regard to compactness and cooling of the window, K, without having a wax seal separating vacuum from water far outweigh this disadvantage. It has been found indeed that at the pressures at which high light intensity is obtained from the tube, the sputtering of the window is not serious, and even when it is necessary to clean the window this is not a difficult operation. It is possible that the small amount of sputtering observed would be reduced by changing the internal form of the electrode (opposite the window) or by using a small quartz cone, as Kistiakowsky (3) did.

In conclusion the advantages of this type of tube may be summarized:—

1. All parts exposed to the discharge are cooled by a compact water-cooling system.
2. The tube is cheap and rugged, and is easily assembled.
3. The water-cooled capillary is an independent unit which may be altered in length if desired, the same electrodes being used.
4. Light escapes from the lamp only along the axis.
5. The lamp can be sealed easily to a vacuum system without loss of distance from the light source.
6. No wax seals separate water from the evacuated system, and all wax joints are far removed from the discharge and water-cooled.
7. The window is efficiently cooled and is easily removed and replaced. It is held in place by a washer and nut, so that in case of fracture of the water-cooled capillary it is not likely to be forced out.

Acknowledgment

The writers are indebted to Mr. G. Tweeddale for mechanical assistance.

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A PLOTTER FOR HIGH OBLIQUE AIR PHOTOGRAPHS[1]

BY E. L. M. BURNS[2] AND R. H. FIELD[3]

Abstract

A machine for plotting maps from high oblique air photographs has been developed under the direction of the Associate Committee for Survey Research. It is designed for use in mapping to the small scales which meet ordinary Canadian requirements, and is not intended to compete with the more elaborate machines now in use for large-scale mapping.

A short description of the plotter is given, and is followed by an account of two experiments, in the first of which it was used to produce a contoured map by a method that involved establishing the position of the camera at exposure from control points fixed by ground survey. In the second experiment the planimetry of a typical area in northern Canada was plotted, with no control other than altimeter elevations of the aircraft, and the elevation of a large lake. The time expended on these experiments was recorded, but in view of the experimental nature of the work and the need shown for minor improvements in the machine, these results are not a true measure of the efficiency that may be developed in practical mapping.

Introduction

For some years Canadian survey officials have been investigating the optical-mechanical plotting of air photographs. The machines that have been developed in Europe and whose principal application is in the production of large-scale maps are inherently unsuitable for economically producing the small-scale maps chiefly in demand in this country. But there appears to be a field for simpler devices, extending or replacing the methods that have been practised in the mapping of considerable areas of the Dominion (1).

Two years ago an Associate Committee on Survey Research was formed under the aegis of the National Research Council, on which committee all Federal Government services interested in survey were represented. The machine here described was first suggested by Major Burns, and subsequently developed by a subcommittee of this committee. It is to be regarded as an initial experiment in the use of plotting machines under the conditions governing mapping in Canada.

Purpose

The High Oblique Plotter is simply a mechanical solution of the projective transformation of single, inclined photographs which include the horizon in the field of view. It is adapted for measurements of the horizontal and vertical angles which objects in the field subtend from the exposure point, and so can be applied to the resection in space of the camera station (exposure point, or perspective centre). If the same detail is visible in two photographs, the goniometric measurements can be used to extend control into inaccessible areas. The machine will also plot the position of detail, such as the shores

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Contribution from the Department of National Defence, Ottawa, and the National Research Laboratories, Ottawa, Canada.

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of lakes, streams, roads, etc., if the ground plane is sufficiently horizontal for errors arising from elevation differences to be disregarded. There are large areas in Canada where this can be done in mapping on the 1/253,440 scale.

Description

Principle

Fig. 1 shows the elements on which the design of the machine depends. S is the lens of the camera at a height H above the ground, and pq is a section of the negative, perpendicular to the line $Sm = f$, through the principal point m. θ is the angle of depression of the photograph from true horizontality. QMP is a horizontal line on the ground. If positives are being considered, pmq is replaced by $p_1m_1q_1$, where m_1 is at a distance f from S. Should a horizontal plane be interposed at a distance h below S, it is easily seen that the distances M_1Q_1 and M_1P_1 are proportional to MQ and MP and, generally, that lines through S and points on the photograph will intersect the plane $Q_1M_1P_1$ so as to reproduce, on a reduced scale, $\left(\frac{h}{H}\right)$, the correct relative positions of the homologous points on the ground.

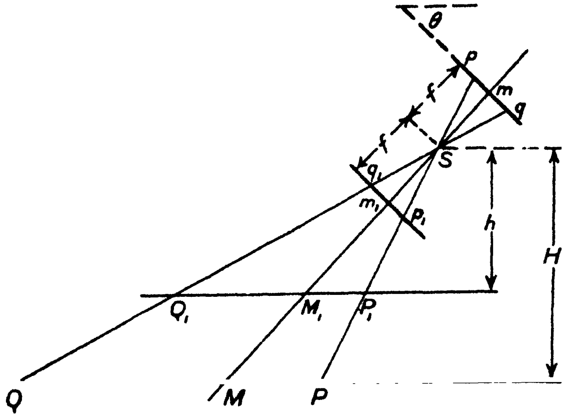

FIG. 1.

Most, if not all, photogrammetric plotting machines of the direct observation type embody (i) a telescope by means of which the direction of a perspective ray may be re-established in space by observing a correctly oriented photograph, and (ii) a space rod, coupled to the telescope and/or photograph in such a way that as the telescope is directed upon an image the space rod moves a tracer which plots the corresponding ground plan of the homologous point.

In this particular instrument the operation is simple, in that the telescope and space rod are connected by a parallelogram linkage so as to remain always parallel to each other, while both follow the direction of the perspective rays. The intersection of the axis of the space rod on a horizontal plane will, therefore, be the ground plan of the point on whose image the telescope is directed.

Construction

The plotter is shown diagrammatically in Fig. 2 and photographs of it are reproduced in Figs. 3 and 4. In Fig. 2, *AB* is the vertical axis of the machine, rotating on a ball-bearing pivot at *B* and constrained by a ball-bearing journal at *C*. *AD* is the telescope, movable about a horizontal axis intersecting and rotating with *AB* at *A*. *EFG* is the space rod, movable about a horizontal axis intersecting and rotating with *AB* at *F*. The link *DE* completes a parallelogram. A screw *HK* on a horizontal slide rotating about *AB* with the parallelogram, operates a nut at *G*. The space rod passes through a sleeve pivoted to the nut.

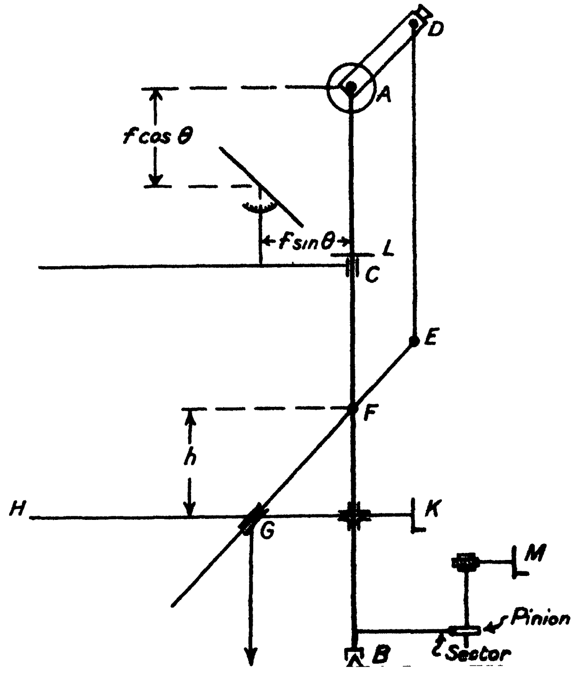

FIG. 2.

The photograph is fastened by clips to a platten, adjustable to permit the angle of tilt, θ, and the vertical and horizontal components of the known principal distance to be set, the last two in reference to the axis at *A*. Similarly the height of the slide carrying the screw *HK* and the sleeve *G* is adjustable, permitting the distance *h* to be set correctly for the desired scale of plotting. Scales and verniers are provided for the control of these adjustments.

It is easily seen that if the telescope is directed on the image of a point in a correctly set photograph of flat horizontal terrain, the intersection of the axes *EG* and *HGK* will be the ground plan of the point to the scale set. For convenience this point of intersection is projected mechanically to the base of the plotter, where a pencil marks the position of the point being observed.

FIG. 3.

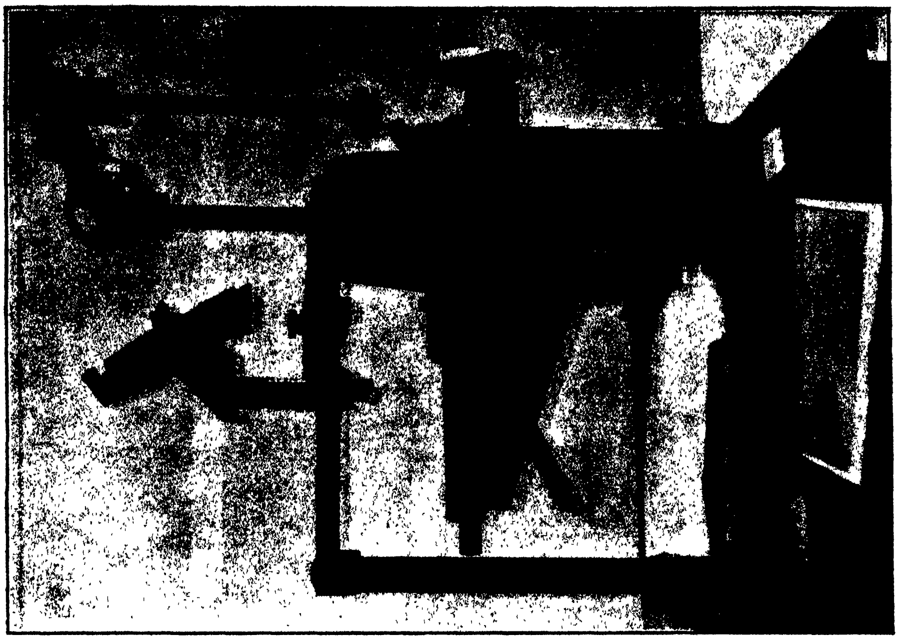

FIG. 4.

Two views of the High Oblique Plotter.

In operation the observer controls two handwheels, *K* and *M*. *K* moves the nut and sleeve *G* horizontally, while *M* rotates the parallelogram, slide, etc., about the axis *AB*, through the medium of a worm wheel and a pinion and sector. Cork inserts in the base permit paper or tracing cloth to be held in position. Graduated circles at *A* and *L* are fitted to measure vertical and horizontal angles subtended at *A* by points imaged on the photograph.

Some consideration was given to the adoption of the Porro principle (2, p. 152), but as the angular errors due to lens distortion were computed to be less than one minute, except near the edges, the simple telescope was adopted. With the low power used (about ×3) very little focusing is required.

Errors due to film and paper shrinkage, often different in the horizontal and vertical directions, may be more serious, but by adjustment of the photograph carrier to the equivalent principal distance in the important direction most of the trouble can be avoided. For example, when horizontal angles are required for resection, the principal distance is adjusted according to the shrinkage factor of the long dimension of the photograph.

When the machine was constructed a jig was made for setting the principal point on the centre of the platten and at the same time bringing the image of the horizon to horizontality. This jig may be seen in Fig. 3 in position for adjusting the air photograph. Subsequent experience with the plotter showed that the setting could be controlled equally well, and more quickly, with the aid of the telescope; consequently the jig was discarded.

Improvements

While the machine fulfilled expectations as to precision and general facility of operation, the initial experiments described below indicated the desirability of some improvements which it is hoped to incorporate before further experiments are made.

Goniometry. The measurement of depression angles is too slow, and would be expedited if the telescope were made so that it could be uncoupled from the link *DE* and provided with a clamp and tangent screw or equivalent device. Azimuth angles can be set quickly by operating the handwheel *M*.

Adjustment for scale of plotting. A screw should be provided so that the scale setting for the height of the slide *HK* can be more readily effected.

Scales. For convenience all scales should be readable from one side of the machine and provided with magnifiers.

Photograph carrier. The photograph carrier was designed with a view to the simplest construction possible. Experience has shown that a more elaborate carrier would be desirable. It is proposed to retain the present carrier for pictures of other than 8 in. principal distance and to construct a new carrier for this distance, as the main use of the machine will be with 8-in. photographs. The proposed carrier will be supported from two vertical arms on the main yoke frame of the machine, the angle of tilt will be set directly about an axis intersecting *A* (Fig. 2) and the principal distance will also be set directly. A special feature of the proposed carrier is a table rotating about the principal point, permitting radial (position or swing) angles to be observed. Angles subtended at the principal point are of special significance in the calibration of tri-camera sets for oblique photography and in the radial line method of plotting vertical photographs. This swing adjustment will also facilitate the setting of the photograph relative to the horizontal. It is also suggested that the new carrier be made with a glass centre, permitting the observation of films and transparencies in the machine.

Experiments with the High Oblique Plotter

Two experiments in which maps were produced with the aid of the plotter were conducted by the Geographical Section, General Staff, Department of National Defence, Ottawa. A description of these follows.

First Experiment: Meach Lake Area

The first experiment carried out was the contouring of a piece of hilly country near Ottawa. The map produced is shown in Fig. 5, which also indicates the system of photography. Pairs of stereo obliques were taken at intervals of about one mile, at right angles to the flight line, which was parallel to Meach Lake—Old Chelsea. Every fifth photograph was taken at 45° to the line of flight, to give intersections for position. The camera used was a Williamson Eagle *Mk* II, 7 × 8 × 8.29 in. (*f*). It was carried in an "Eyrie" mount, which for the map maker's purpose had the disadvantage that the long side of the photograph was vertical, thus giving a narrower angle for resection of the exposure position.

Primary control consisted of a traversed and leveled road in the foreground, and a number of points in the background (five to eight miles distant) consisting of road corners, etc., in the plain lying to the other side of the hill ridges.

The first step was to select the points that would be needed as control for contouring under stereoscopic examination, and mark them on three photographs, including one taken at 45°.

The photographs were then set in the plotter, the angle of tilt having been computed from the visible horizon. Readings of vertical and horizontal angles were taken to control points, usually at least four, one pair in the foreground and one pair in the background. The directions to these points were plotted by the machine on tracing paper, which was used for resection of the plumb point. The height of the aircraft was then computed from the vertical angles to the control points, and the horizontal distances. Usually small errors in tilt and swing setting were disclosed, which allowed the necessary corrections to be simply computed. Captain D. Crone, R.E., of the Survey of India (4) and Mr. O. M. Miller of the American Geographical Society (3) have both furnished solutions for this problem. The photograph was reset, in accordance with the corrected tilt and swing, and check readings were taken

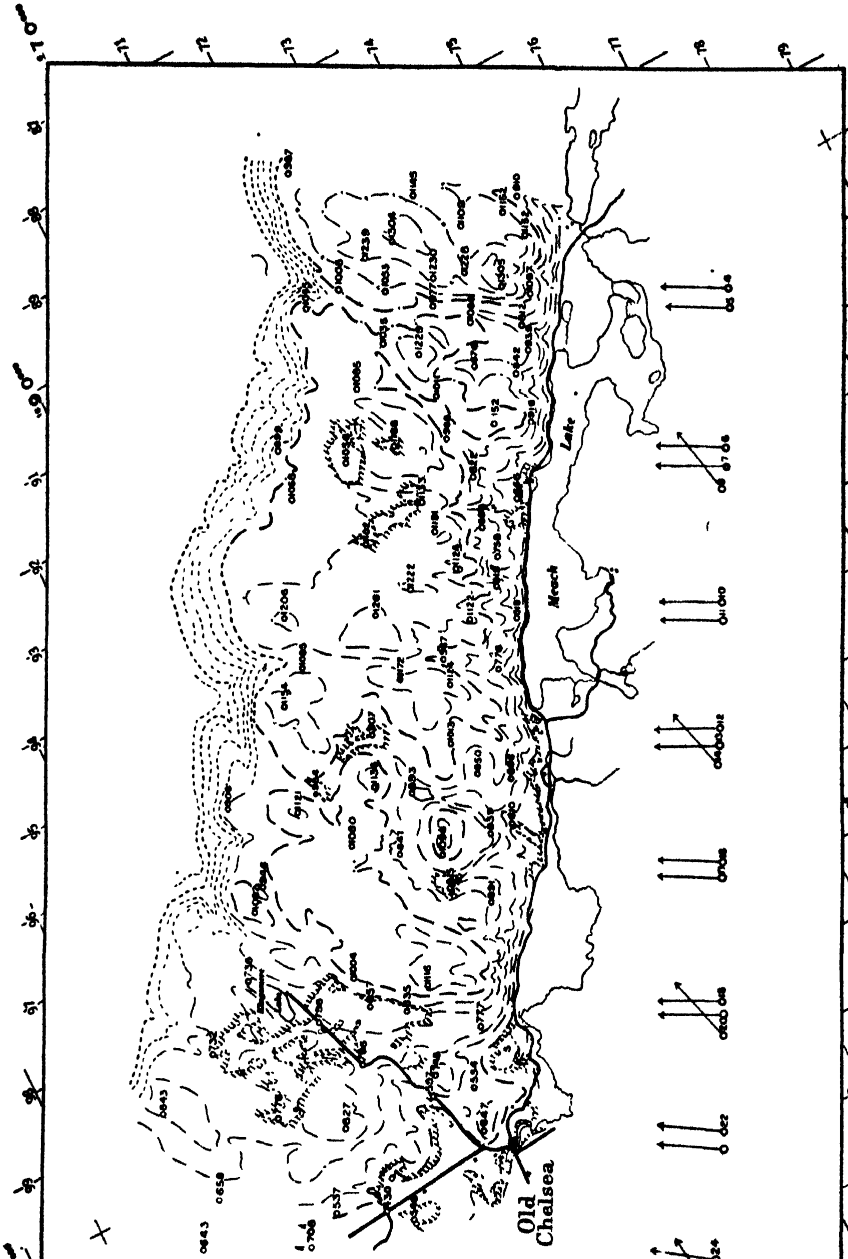

FIG. 5. *Contour map of the Meach Lake–Old Chelsea district near Ottawa, plotted by means of the High Oblique Plotter.*

to the control points. When the heights of the exposure point as recalculated showed a satisfactory agreement, vertical and horizontal angles were measured to all the contouring control points which had been marked on the photograph. The points were also plotted on a piece of tracing paper in the machine, but as their heights were unknown, these plotted positions gave directions from the plumb point only.

When several photographs had been measured in this way, the plots on tracing paper were laid down on the control sheet, on which the photograph plumb points had already been marked, and the intersection of the rays to the height control points gave their plan positions. The heights of the points were then computed from three photographs. Agreement of the three values showed whether there were any serious errors in the operation.

After all the control points had been heighted, the photographs were contoured under a stereoscope. It may be mentioned that stereo obliques, owing to their necessarily smaller bases, provide an impression of relief much inferior in comparison to the usual verticals; this resulted in the interpolated contours being considerably poorer than the contouring would have been on vertical photographs with the same number of spot heights. The final step was to plot detail and contours of each photograph in the machine, and compile these plots on the control sheet.

Methods of Checking and Results

The finished map was checked by fixing hilltops and other prominent detail by plane table intersection and heighting by Indian clinometer; also by traverse with batteries of aneroid barometers, corrected by stationary barometer readings.

It was soon apparent that the heights of the control points fixed from the photographs were quite good, but that the height representation by contours in areas where there were no spot heights was less satisfactory. In checking, it was not easy to identify positively on the ground the points which had been heighted from the air, which might, for instance, be distinctive trees, etc. However, some forty points were identified and checked, and the results showed that the "probable error" of the method was ±15.6 ft. A number of other points, a few hundred yards from the photograph control points, were heighted, and the heights compared with the elevations shown by contours. The results of this series combined with the first showed a "probable error" of ±25.6 ft., the large increase being due to two errors of over 100 ft.

The object of the experiment was to provide a method of contouring at a 100 ft. interval from oblique photographs, suitable for a limited area. So far as accuracy is concerned, this object could be said to be attained, the resulting map being about of the same standard as those of similar country done by ground methods. As regards the time required, the result was less satisfactory, about twenty days having been needed for the work, which covered only 15 sq. miles; *i.e.*, considerably longer than it would take if done by plane table. Of course, it was the first attempt with the method, and it is probable that, with certain minor improvements in the machine and with further experience, the time might be cut down to 10 or 12 days. Furthermore, more useful results might be obtained in more mountainous country, where the relief would run up several thousand feet, instead of some eight hundred, as in the Meach Lake area.

It is, however, clear that no method of detailed plotting and contouring hilly country from single photographs, in which points have to be identified separately, will be able to compete in economy and accuracy with stereoscopic methods. And furthermore, it is probable that vertical photographs taken with multi-lens cameras will largely supplant the high oblique for small-scale mapping in Canada. But there may remain certain uses for oblique photography in obtaining spot heights in inaccessible country.

Captain Crone (4) has developed a method of dealing with the case where some comparatively distant control points for the photographs, in inaccessible territory, can be obtained by instrumental intersection from the ground. But maps might be required of areas where such distant instrumental control would not be possible,—as when a ridge interposed between accessible territory and the ground it was desired to map. In such a case, it might be feasible to use a method employing obliques, taken simultaneously with three coupled cameras, similar to the following.

Coupled oblique photographs are taken as in Fig. 6, so that the area each set covers lies partly in accessible territory and partly in inaccessible territory. The control points in accessible territory would permit the resection of the exposure position, and also enable the tilt of the triple photograph to be computed in the directions parallel to, and at right angles to, the "boundary". Rays could then be projected to intersect at suitable points for control in the inaccessible territory. In principle, the rays projected to the unknown points should be balanced by rays of equal length projected to known points.

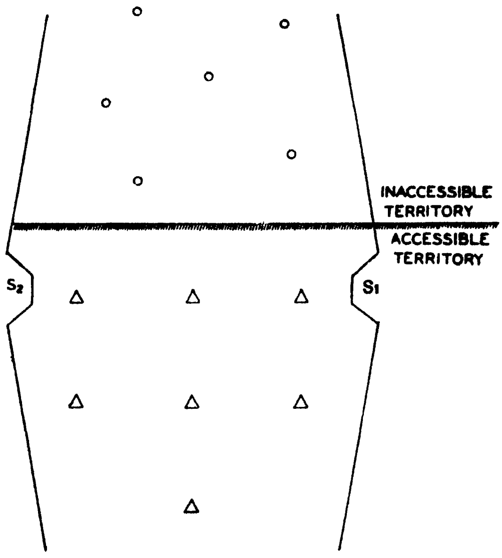

FIG. 6.

The accuracy attainable with this type of aerial triangulation would depend on various factors:—limits of accuracy of the goniometer; the distortion in photographic materials; resolving power of the lens and emulsion; the visibility when the photograph was taken; and the character of the object chosen for intersection, considered as a target.

Experiments in this type of control extension into inaccessible country are being put in hand in Canada. It is intended only to fix a minimum of control points by this means, planimetry and relief detail being filled in from stereo verticals.

SECOND EXPERIMENT—GREAT SLAVE LAKE

The coupling of three cameras has provided the means for strengthening the plotting of oblique photography. Previously the three photographs of a "fan" were taken in rapid succession with the same camera; they had, therefore, separate exposure points, though the planimetry plotted from them could be tied together through the overlap to a sufficient degree of accuracy*. Direction of the series was maintained by azimuth lines passing as nearly as possible through the plumb points of the centre pictures and continued from one picture to another.

Now, however, the three coupled cameras are exposed at the same time, and hence have a common exposure point. They can also be calibrated so that the angular relations of their optical axes are known. The result is that one may plot a sector of ground covering about 165° in plan and extending to the limits of visibility, as if it were all on one photograph. With this wide angle of view, given suitable control, strong resections may be made. And with several parallel lines of photographs, a system of resection and intersection may be worked, to give a good aerial triangulation, in a manner similar to the radial line method with verticals.

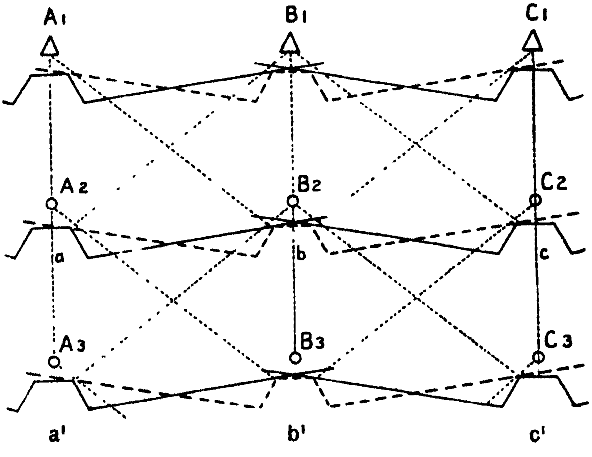

FIG. 7.

In Fig. 7, A_1, B_1 and C_1 are control points fixed by ground methods; a, b, c are each triple photographs resected from this control by the rays shown in dotted lines. Then A_2, B_2 and C_2 are intersected from a, b and c. a', b' and c' are then resected from the points already established, and A_3, B_3 and C_3 intersected, and so on.

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*For details of plotting methods see Reference (1).

It will be seen that such a triangulation can give accurate results (within the limitations of graphical methods) despite differences of elevation in the ground being mapped. This would be a considerable advance on the original high oblique method, where it has to be assumed that the ground being mapped is a horizontal plane. When it was *not* a horizontal plane, scale and position errors arose.

In plotting country where elevations differ to any great extent, it would be necessary to intersect all detail, in order to fix its position correctly. But in Canadian practice, where detail consists mostly of lakes and rivers, the drainage gives clues to levels which enable the detail to be adjusted to its proper position without such a multitude of intersections.

As an experiment in this method, an area at the east end of Great Slave Lake was plotted with the High Oblique Plotter. Conditions were not the ideal ones shown in the diagram; the lines of photographs were, so to speak, in echelon, instead of being abreast of one another. As suitable control was not available, the plot was started by working along the shore of Great Slave Lake, and using the points so fixed for subsequent resection of the inland photographs.

Some 325 sq. miles in all were plotted, and so far as it is possible to judge without check on the ground, the method suggested above is a practicable one. The resulting plot is shown in Fig. 8. It was found that certain alterations of the machine (as already mentioned) would be desirable, in order to increase speed and accuracy of working; but, in essentials, the apparatus will do what was expected of it. Resections and intersections fitted well, and the shapes of features were accurately rendered in plotting, the latter fact being proved by the agreement of plots of the same feature from different photographs.

The production of a map could, it is estimated, be carried out at a rate of about three square miles per working hour. The actual plotting of detail on a single photograph, which usually covers about six square miles, takes about thirty to forty-five minutes, including setting the photograph. It is considerably easier to plot distant features than with the perspective grids, and the result is more accurate.

Acknowledgment

The authors wish to acknowledge assistance and advice given by other members of the Subcommittee on Mapping Methods. The shop drawings for the plotter were prepared in the Division of Physics and Engineering of the National Research Laboratories, and the machine was constructed in the instrument shop of the Laboratories by Mr. W. C. May, of the shop staff, who contributed many valuable suggestions during the course of the work. Mr. R. D. Davidson of the Geographical Section, General Staff, carried out the calculations and plotting for the experimental maps, assisted by Sergt.-Majors Cruickshank and MacDonald, R.C.E., and much credit is due to them for their careful observations.

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DIRECTION FINDING OF ATMOSPHERICS[1]

By John T. Henderson[2]

Abstract

The results of one summer's observation with a cathode ray direction finder and an automatic recorder to locate the bearings of atmospherics are given and discussed.

It appears that storm areas or areas of low barometric pressure are responsible for many of the observed atmospherics. The feasibility of utilizing the method as a means of weather forecasting is suggested.

The important and deleterious influence of atmospherics upon radio signals has been recognized since the earliest days of wireless communication, and of late considerable attention has been paid to the meteorological conditions that appear to influence their origin and behavior. One method of attacking the problem, developed principally by the Radio Research Board of Great Britain, has been to study the individual atmospheric. Amongst other properties examined the azimuthal bearing of each atmospheric has been observed and recorded simultaneously at two stations separated by a long distance on the earth's surface. It is thus possible to state the point of origin of each atmospheric after making reasonable assumptions regarding its propagation. Hence by determining the points of origin of a large number of atmospherics, a statistical examination can be made of any correlations that may exist between the source and local or general weather conditions.

Prompted largely by the success of the work in Great Britain, it was decided to carry out preliminary observations with a similar direction finder to acquire some experience of local weather conditions, and to determine the value of establishing two such stations in Canada.

Apparatus

(a) *Cathode Ray Direction Finder*

The apparatus used was designed and constructed by the Radio Research Board of Great Britain and is a duplicate of the apparatus in use there. The cathode ray direction finder, which is the instantaneous reading instrument used to determine the bearings of individual atmospherics, has been adequately described (6). The principle of its operation is briefly as follows: Two frame aerials are mounted with their planes vertical and oriented one in a north south direction and one in an east-west direction and adjusted so that the loops are electrically, as well as geometrically, at right angles to each other, to ensure that there is no mutual effect of one loop on the other. If an incoming signal makes an angle θ with the meridian, the voltage in the frames will be $k \sin \theta$ and $k \cos \theta$, where k is a constant. The signals picked up by the two frames are amplified by two identical amplifiers having equal gains

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[1] *Manuscript received August 31, 1935.*
Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

[2] *Physicist, National Research Laboratories, Ottawa.*

and imposing equal phase displacements on the incoming signal, so that the ratio of the outputs of the two receivers is identical with the ratio of the input. The signal from the north-south frame, after amplification, is impressed on the vertical deflecting plates of a cathode ray oscillograph, and the signal from the east-west frame is impressed on the horizontal deflecting plates of the oscillograph. The oscillograph spot will thus be deflected in a direction making the same angle with a vertical deflection that the original signal makes with the north-south meridian, namely, θ degrees. The receivers are superheterodynes and the beat oscillator is common to the two units, this being a necessity if phase relations are to be preserved. A test signal can be injected into the frames to check the equality of the amplifiers. The gain can be altered over a wide range, and an adjustment to ensure phase equality at all gains is provided. The face of the cathode ray tube can be calibrated so that each deflection indicates the bearing of an atmospheric instantaneously. A protrator circle, drawn on the oscillograph tube, is marked at 10° intervals by impressing voltages whose magnitudes are proportional to $A \sin \theta$ and $A \cos \theta$, in 10° steps, from a special potentiometer, and the instrument can thus be used for direct reading visual observations.

The observational procedure is to adjust the receivers at some suitable value of amplification determined by the frequency of the atmospherics and to photograph them as they appear on the cathode ray tube. A lens focuses the spot on a moving film so that the record is a series of lines at various angles indicating directly the bearing of the atmospheric (see Fig. 1; the reproduction lacks much of the contrast obtainable when the film is projected), the zéro position of the spot being masked, as the north-south deflections would not otherwise show on the record. The film having been run downwards for about a minute, it is moved transversely and run upwards.* Three or four traces can be obtained in this way, resulting in considerable economy of film. If more than one observing station is being used, then exact synchronism of observation is essential, but for the single station observations here discussed, it suffices to make the observations daily at about noon. The observations suffer from the usual 180° ambiguity of other direction

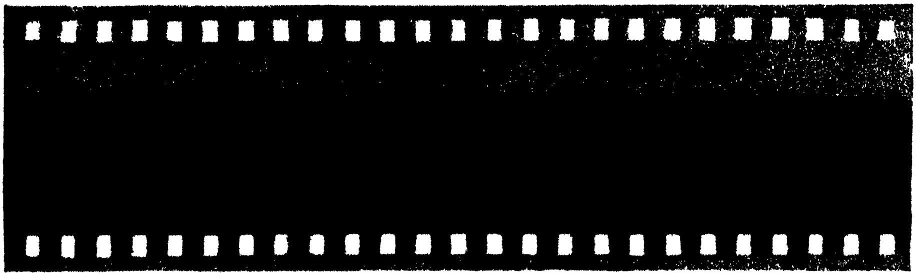

FIG. 1. *Sample C.R.D.F. Record.*

finders, and from the customary site errors and propagational errors of any direction finder, although the last two are minimized by the very long wavelength used (30,000 metres).

(*b*) *Recorder*

Supplementing these determinations on individual atmospherics, an automatic recorder, also constructed for the author by the Radio Research Board of Great Britain, was used to give an indication of the predominant direction of arrival of atmospherics, and to follow the movements of the major source, or sources. In this instrument two frame aerials are arranged 90° apart, with their planes vertical and so that they can both rotate about the same vertical axis. The loops are turned by a clockwork motor at a rate of four revolutions per hour. The signals induced in these frames are amplified through two similar amplifiers. The pen of a mechanical oscillograph moves up and down and makes a trace on a piece of paper placed over a drum. This drum is driven synchronously with the rotating frames, and for each rotation travels a small distance axially downwards, so that the trace of the pen if undisturbed would be a spiral traced on the paper. The pitch is such that the lines are nearly parallel to the bottom edge of the paper when it is removed from the drum.

The signals from one amplifier, called the opposing set, move the pen downwards; those from the other, the recording set, move the pen upwards. A stop is fitted to inhibit motion of the pen downwards and the resultant combination gives a direction finder that will accept signals only over a narrow sector. To remove the usual ambiguity of 180° the signal from a vertical aerial is added to that of the recording frame, making due allowance for the phase shift of 90° required, thus giving the familiar cardioid diagram type of response. The net result is an unambiguous direction finder accepting signals over about 40°. The charts are changed daily and little attention is required.

Results

Preliminary tests in October, 1933, having shown that the main laboratory of the National Research Council was an unsuitable location for the direction finders, they were installed during the early part of January, 1934, in two field huts at Rockcliffe Aerodrome, about six miles outside Ottawa. Although this site is not an ideal one, it was the only place available at the time. A few observations were made during the winter but it was found impossible to start regular work until the middle of May.

During the period May 25 to August 7, an attempt was made to take daily observations, Sundays excepted, at approximately eleven o'clock in the morning (Eastern Standard Time). Observations were made on 57 of the 63 working days, and on some favorable occasions it is possible to deduce the sense of the C.R.D.F* observations from examination of the recorder charts. Unfortunately this is definitely possible for only 28 of the 57 days.

**This abbreviation is used throughout for cathode ray direction finder.*

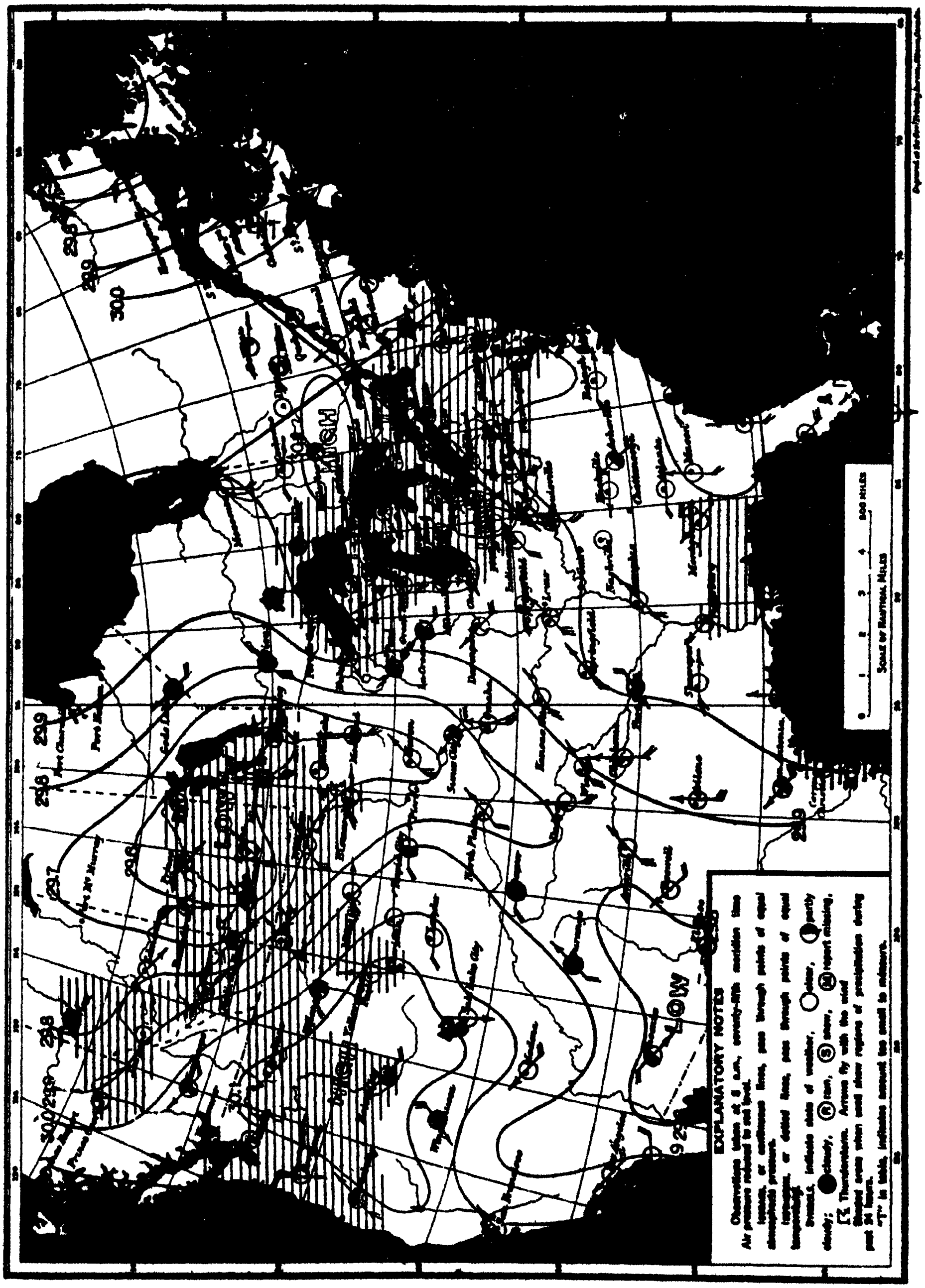

FIG. 2. *Principal directions, observed June 27, 1934.*

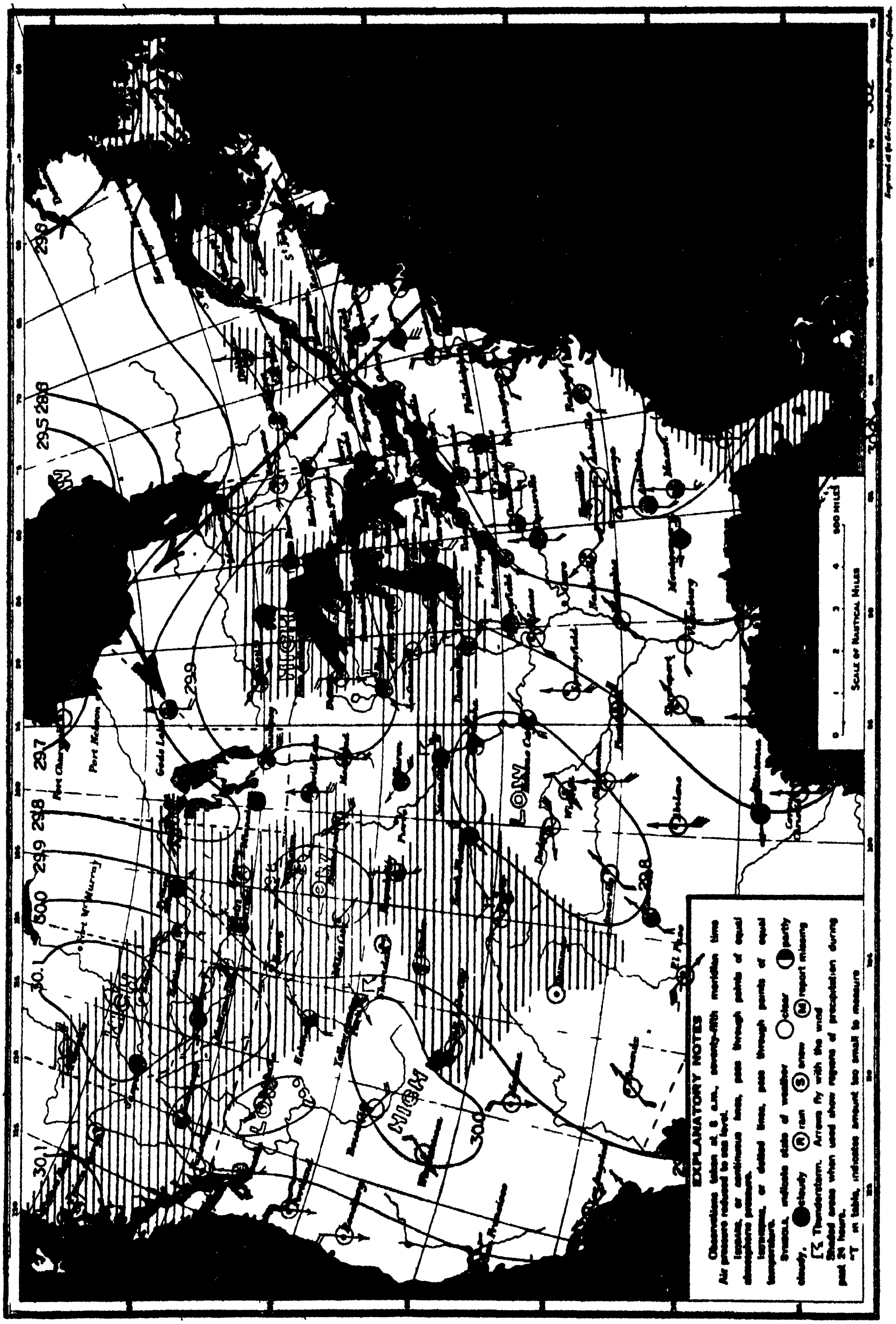

FIG. 3 Principal directions, observed July 5, 1934.

The atmospherics were photographed for four minutes. With the amplification customarily employed this provided a large number of data, the reduction of which is rather laborious, as the film must be projected and the bearing of each atmospheric determined separately. Although the time of observation may appear to be short, it is felt that it was long enough to give a good idea of the predominant conditions existing at 11.00 a.m. each day, and hence, to compare conditions as they exist from day to day.

As a rule the bearings so found can be grouped around half a dozen directions with a dispersion of only a few degrees. These in turn generally resolve themselves into one or two principal directions that are more or less a mean value for a much larger dispersion of readings. The departure of individual values from these principal directions may be large (about 15°) but, because observations from only one station are available, it is thought better to consider these rough averages, rather than attempt at present to deal with the more sharply defined directions, each consisting of a much smaller number of observations. The sense of the principal direction can be given only in a limited number of cases.

These principal directions can be plotted on a map* and the indications compared with the general weather conditions. When this is done it is found that the directions usually pass through, or close to, a low pressure area. Often when two principal directions are found they both point to the edges of such a region, such that if the low were a circle, the lines would be two tangents to this circle from Ottawa.

An example is seen in Fig. 2 which shows the results for June 27, 1934. In this case the principal directions have simply been drawn in roughly on a weather map to illustrate the point. Obviously great circles are not straight lines on such a projection as this one, but the method is good enough for a pictorial representation of what is happening. The sense of the more prominent source, judging from the number of atmospherics and the recorder chart, is indicated by the arrow and points to the Lake Ontario–Lake Erie region. Numerous thunderstorms are indicated on the map for this locality, so that the storms are undoubtedly the points of origin of the disturbances. In this case the second direction drawn on the map is not easily interpretable, as a number of possibilities might be taken, but the weather map for the following day shows thunderstorms in the vicinity of Cochrane, so that it is probably northwesterly.

A second example is shown in Fig. 3. Here the principal direction points to the edge of a low, which would lead one to expect the area to be moving with this as the leading edge, because this is frequently the case. Actually the low was moving in the direction shown by the arrow at the top of the page.

Table I gives the results in synoptic form for the period under review. The bearings are given in Column 3 and the area that appears to be associated with the atmospherics is indicated in Column 4, together with an approximate

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**Daily weather map prepared by Dominion Meteorological Service.*

TABLE I

SUMMARY—C.R.D.F. OBSERVATIONS

Date	Obs.	Azimuth	Probable source of atmospherics
May			
25	*a*	5°	Low, moving north with thunderstorm (Norfolk, Va.)
26	*a*	35°	Low, moving north
27	*M*	—	
28	*a*	155°P_1; 75°P_2	(Low moving W. by N.)P_1 (?)P_2
29	*M*	—	
30	*a*	165°P_1; 35°P_2	Lows and thunderstorm
31	*a*	132°P_1; 60°P_2	(Advancing low)P_1; (Low, centre of)P_2
June			
1	*a*	165°	Seems to be high *or* edge of moving low. *Doubtful*
2	*a*	—	Directions scattered. Low centered over Ottawa
3	*M*	—	
4	*M*	—	
5	*a*	65°	(Thunderstorm and low edge), same direction + 180° = low
6		65°P_1; 160°P_2	(Thunderstorm, Lake Erie)P_1, many small X's; *Local thunderstorm*
7	*M*	—	
8		115°	Low edge—NOTE: High centered over Ottawa
9	*a*	105°	Local tunderstorm (Low centre, near Duluth, and thunderstorm)P Many thunderstorms shown over Great Lakes area
10	*M*	—	
11		120°P_1; 90°P_2	(Between two lows)P_1. (Low edges)P_2 and P_3 (This low moving east towards Ottawa, directions to two advancing sides of same area)
12		35°P_1; 165°P_2	(Low edges)P_1 and P_2
13		130°P_1; 85°P_2	Local thunderstorms and low over Ottawa (Low edge)P_1 (Low centre)P_2
14	*a*	105°P_1; 20°P_2	Low edge
15	*a*	85°	(Low near Nova Scotia) or (Thunderstorms near Kansas City and North Platte)
16	*a*	107°P_1; 20°P_2	(Low edges and thunderstorms) or (Low centre)
17	*M*	.	
18	*a*	40°P_2; 135°P_1	(Low and low edge) or (two high centres)
19	*a*	55°P_1; 110°P_2	(Low edges)
20	*N.B.*	160°	Runs between high and low area—*doubtful*
21		55°	Local thunderstorms, low centre near Ottawa; (Lakes Ontario and Erie)P_1; thunderstorms prevalent on Lower Lakes
22			Recorder points to low edge
23			*No. C.R.D.F.* Recorder points to high centre but low and thunderstorms at 180° away
24	*M*		
25		75°P_1; 115°P_2	(Low and thunderstorms)P_1; (Through high to low edge and thunderstorms)P_2
26		135°P_1; 75°P_2	(Rainy regions near Boston)P_1; (Low edge near Erie *or* low edge near Anticosti)P_2
27		145°P_1; 55°P_2	(Low near Detroit, thunderstorms)P_1 (?)P_2
28		45°P_1; 145°P_2	(Vicinity N.Y. City; thunderstorms near Norfolk)P (Low or Lake Erie)P_2
29		105°P_x; 135°P_y	(Thunderstorms, near Duluth)P_x; (Thunderstorms near Boston)P_y
30		75°	Low over Newfoundland
July			
1	*N.B.*	65°P_x; 145°P_y	(Lake Erie)P_x (N.Y.City, thunderstorm near Norfolk)P_1 (directions + 180° point to edges of one low) *doubtful*
2	*M*		
3		135°	(Low edge or Boston and rain)—A few thunderstorms reported elsewhere
4		55°P_1; 165°P_2; 105°P_3	(Thunderstorm, N.Y. City)P_1; (Thunderstorm, Boston)P_2 (Thunderstorm, Lower St. Lawrence)P_3
5		155°	Low edge
6		135°P_1; and 45°P_2	(Low edge, distant)P_1; (Thunderstorms over Lake Erie)P_2
7		80°P_1; 135°P_2	Low edges

TABLE I—*Concluded*

SUMMARY—C.R.D.F. OBSERVATIONS

Date	Obs.	Azimuth	Probable source of atmospherics
8	*M*		
9		65°P_1; 170°P_2	(Lake Erie; rainy)P_1 (N.Y. City, rainy)P_2
10		Possibly 170°P_2	Directions varied, possibly low
11	*N.B.*	125°	(*Distant low.*) Misses many thunderstorms on Lakes Ontario and Erie
12		170°	(Distant low). Misses many thunderstorms on Lower Lakes (Local thunderstorms predicted both July 11 and 12)
13	*M*		
14		145°P_1; 55°P_2; 15°P_3	(Low, Norfolk)P_1; (Thunderstorm, Lake Erie)P_2; (Low edge)P_3
15		55°P_1; 145°P_2	(Low off coast N.Y.)P_1 (Gulf of St. Lawrence thunderstorms near Cape Breton Island and low centered north of Gulf; but same directions + 180° Lower Lakes and thunderstorms)P_2
16		95°P_1; 165°P_2	(Thunderstorms in Maritimes)P_1 (?)P_2
17	*a*	75°P_1; 135°P_2, 20°P_3	(Thunderstorms over P.E.I.)P_1 (Thunderstorms near Norfolk)P_2; (?)P_3
18	*a*	5°P_1; 105°P_2 (155°P_3)	(Norfolk, rainy, edge of high)P_1; (Thunderstorms, St. Paul, Wis., or low edge, N.S.)P_2
19		125°P_1, 5°P_2	Thunderstorm and low, Port Arthur, Ont.
20		65°P_1; 15°P_2	(Thunderstorm, Lake Erie)P_1; (thunderstorms in Laurentians, north of Quebec City)
21		165°P_1; 55°P_2	(Low near Detroit)P_1; (N.Y. and rain)P_2
22	*M*	—	
23	*a*	155°	(Low near Norfolk) or high
24	*a*	95°P_1; 145°P_2	(Through high to receding low)P_1; (Advancing low)P_2
25	*a*	155°P_1; 75°P_2	(Advancing low of 24/7/34)P_1 (?)P_2
26	*M*	—	
27	*M*	—	
28	*M*	—	
29	*a*	145°P_1; 35°P_2	(Edge of low)P_1 and P_2 *or* (N.Y. City, rain)P_1; (Atlanta, Ga., thunderstorm)P_2
30	*a*	20°P_1; 140°P_2	Low centered over Great Lakes. P_1 and P_2 probably to edges of this low
31	*a*	145°	(Thunderstorms and low)
Aug.			
1	*a*	145°P_1, 25°P_2	(Thunderstorms near N.Y. City)P_1; (low)P_2, *probably*
2	*a*	135°P_1	(Low)P_1; (Thunderstorms over Lake Superior, low centre)P_2
3	*a*	65°P_1 and 155°P_2	(Thunderstorms, Lake Erie)P_1 (Thunderstorm, N.Y. City)P_2
4	*a*	65°P_1 and 145°P_2	(Lake Erie or St. Lawrence and low)P_1; (Low, James Bay)P_2
5	*M*		
6	*M*		
7	*a*	65°P_1 and 145°P_2	(Low)P_1 (Low, James Bay)P_2 (Probable)

Note: M in Column 2 = observations missing. a in Column 2 = ambiguous directions by 180°—no sense.

Where two principal directions P_1 and P_2 were found, the locations of the corresponding sources are shown as (Source 1)P_1: (Source 2)P_2

When one direction only is given for the ambiguous cases, only the more probable direction is shown.

indication of its position. When more than one principal direction was observed the probable source of each is indicated, the various directions being differentiated by suffixes, as P_1, P_2, etc. (The numerical incidences on one or two days being about equal from two sources, they are simply called P_x and P_y.) When an alternative source is indicated for a given direction this refers to the direction observed + 180°, and for these cases the first source given is considered the more probable.

It will be seen from Table I that the sources of the electrical disturbances are apparently located in thunderstorm or low pressure areas. It is well known that thunderstorms produce atmospherics, and lightning is considered by many workers to be their only source. There is nothing in the present series of observations to contradict this viewpoint, for there may have been unreported thunderstorms present. Again it is quite possible that there may have been invisible electrical discharges occurring in areas where thunderstorms were not fully developed, yet which were of sufficient intensity to cause severe interference in a radio receiver. If one assumes that these lows or thunderstorms are the sources of atmospherics, then the correlation shown in Table I is very high.

If one assumes that high pressure areas, rather than low, were associated with the sources of atmospherics, then a much less satisfactory correlation is obtained. In fact, these observations fail to point to thunderstorms or lows in only three instances. On two consecutive days the directions, although pointing to a distant low area in the northwest, show little indication of very much disturbed conditions over the Lower Lakes, where many thunderstorms were reported. It is, of course, quite conceivable that a local storm occurred, though it is not indicated on the map. This would mask the true predominant direction. (Local storms were in fact predicted over wide areas for both days, July 11 and 12.) On the third occasion the sense, as found from the recorder, is exactly opposite to what one would expect (June 23).

If the lack of correlation for the two days be due to local thunderstorms, then the method is obviously one of considerable promise, and the work should be continued with at least two stations and preferably a network of stations over the whole continent. Stations at, say, Ottawa, Winnipeg, and possibly somewhere around Kansas City would give a very good idea of conditions over the inland portions of the continent, and would be strategically placed to observe the conditions around the Great Lakes.

Discussion

The C.R.D.F. used for these experiments is capable of considerable accuracy, this being about ± 1° for individual deflections of the order of three centimetres on the oscillograph tube, decreasing slightly with decreasing deflection of the spot. No account was taken of the site errors of the direction finder, but these would have to be determined in any more extensive program.

Rectilinear propagation is tacitly assumed for all the electromagnetic disturbances, but when the incoming atmospheric has an abnormal component of polarization it will appear as an ellipse on the tube. These elliptical patterns were ignored in the present work, and it is believed that the results are not appreciably affected by so doing, as only about 15% of the traces of the total number of atmospherics observed are not straight lines.

The errors due to abnormally polarized components are discussed by Munro, Webster and Higgs (4), and, although they show from theoretical considerations that very large errors in bearing are possible, they consider that their results (obtained using two stations to locate the source) are not in error by more than 3° for distances exceeding 200 km. Less distant sources can give rise to greater errors but the author is inclined to the opinion that this is not such a serious matter, because the greatest advantage of the C.R.D.F. as a meteorological instrument is its ability to give some indication of conditions over large, sparsely populated land areas or over sea areas, along the coast line, where meteorological information is meagre or non-existent.

To locate a source by triangulation it is, of course, essential to have at least two stations observing simultaneously, and it would greatly facilitate interpretation of the results if the sense of the bearing were indicated. Inasmuch as only one station was used in the present series of experiments we are handicapped in estimating the true location of the source, but where two-station observations have been made, *viz.*, in Great Britain (5, 6), Australia (3, 4), and the United States (1, 2), the results indicate that the foregoing locations of the sources are reasonable and correct.

It is understood that a network of C.R.D.F. stations is to be established around the Gulf of Mexico by the U.S. Navy and by the Universities of Puerto Rico and Florida, for the purpose of locating hurricane areas. The success of the British and Australian results with C.R.D.F. observations lends very strong support to the viewpoint that a network of such stations in Canada would be of use as an aid in weather forecasting, particularly in the unsettled northern districts or off the Atlantic and Pacific coasts. Probably six stations would ultimately be required, but a second station at present should enable the value of the method to be properly estimated. The importance of exact knowledge of weather conditions to the various air services of the country is obvious, and the cathode ray direction finder appears to be a useful aid to the meteorological services. It is hoped that it will be possible to continue the work in the near future.

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OSCILLATIONS IN THE SPARK FROM INDUCTION OR IGNITION COILS AND THEIR SUPPRESSION[1]

BY R. RUEDY[2]

Abstract

In the low-voltage stage of the spark, the current depends on the solution of a cubic equation, and has therefore in general one strong aperiodic and two alternating components. When the ratios $\alpha_1 = R_1/L_1$ of the primary and $\alpha_2 = R_2/L_2$ of the secondary are kept small compared with the natural angular frequency ω_1 of the primary, damped electrical oscillations of frequency $\omega_1(1 - \kappa^2)^{-\frac{1}{2}}$ are set up in the windings, even when the voltage at the spark gap is constant. With larger values of α_2 and if necessary higher coupling factors, κ, the frequency of the oscillations decreases and near the point at which $(\alpha_1 + \alpha_2)^2/3(1 - \kappa^2)\omega_1^2$ becomes smaller than unity, the discharge becomes aperiodic, or under certain conditions, intermittent. Rapid changes of short duration cause the wires leading from the spark to the coil and portions of the coil to oscillate, the leads acting as antennas rather than as circuit elements with uniform distribution of the current. In the aperiodic stage the current behaves as if it were independent of the primary.

Introduction

It is difficult to investigate the current in the spark discharge because in less than a microsecond it may change from the dark stage, or from a brush dicharge, to a glow or an arc. Since ionization takes place along a narrow path, space charges accumulate in such a way that the resistance of the gap rapidly falls from infinity to a low value. Finally the drop in the discharge voltage stops, however, at the potential of the glow or the arc.

The difference between the early, high voltage, and the later, low voltage, stage of the discharge across a short gap becomes enhanced in the case of the ignition coil. When the strong primary current, a few amperes, is suddenly interrupted, or more accurately reduced in strength, the high voltage in the secondary—about 6000 volts for 0.3 mm. gaps—causes breakdown of the air. The rate at which the voltage across the secondary rises from zero to the sparking potential is governed by the intensity of the primary current and the constants of the coil. As a rule, the primary current is so chosen that the voltage produced is much higher than the potential required to break down the gap, since a higher tension sharply reduces the lag between

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the time of applying the voltage and the passage of the discharge. The work dissipated by the spark proper is relatively small; with an average potential of a few thousand volts, a current not greater than a few milliamperes and of a duration of one microsecond, it may amount to not much more than one microjoule or 0.24 microcalorie, whereas the energy stored in the coil is 0.01 joule, even if the primary inductance be only about 0.01 henry and the current one ampere (1, 4). The discharge of the large amount of energy stored in the coil is then completed in the path remaining conductive after the passage of this initial or capacitive stage of the spark, for which the curve obtained by plotting voltage against current drops sharply. In the second, the so-called inductive stage of the spark, the voltage may on the contrary, as many tests have shown, remain perfectly constant, at a few hundred volts, or change only slightly, despite increasing or fluctuating currents. This behavior reveals the fact that the initial spark which fires the combustible mixture in an ignition engine is followed by a true glow discharge (or in some cases, an arc), at atmospheric or higher pressure. The low-voltage stage presents all the components of the glow discharge as they are known from experience with neon tubes; for instance,,the negative glow, the dark space (0.3 mm. wide) the positive column and, in air, a bright reddish anode glow (4, 8).

Since the primary possesses capacity and self-induction in parallel, the sudden break of the current causes electrical oscillations to be set up which are transferred to the secondary circuit. Experience leaves no doubt that the operation of an ignition or an induction coil interferes in general with the reception of radio waves in three very wide regions: (*a*) in the range of short waves higher than 10 Mc. (less than 30 metres wave-length), (*b*) in the entire band from 1500 kc. (broadcasting frequencies) to about 100 kc., and (*c*) in the higher range of audio frequencies.

In order to be able to suppress the vibrations, it is necessary to know where they have their source. Interference in the short-wave region is due simply to oscillations set up at the breakdown of the gap owing to the agreement between the duration of the breakdown proper and the natural period of that portion of the circuit that consists of the spark and the wires, 30 to 100 cm. long, leading from the spark to the ends of the secondary. The current is strongest near the spark and decreases toward the coil, the wires oscillating as half-wave dipoles, so that a small change in their length affects the frequency that is radiated (5). A glance at the constants of the coils used furthermore suggests that the period of the oscillations in the audible range is determined by the coil oscillating as a system of two coupled circuits (1). It remains to examine in more detail the influence of resistance often introduced in the secondary in order to damp the oscillations. The origin of the broadcast frequencies, finally, which in practice are of particular interest, has remained obscure and requires a more complete analysis of the circuit than has hitherto been attempted.

Theory of Audio Frequencies Produced by the Coils

The conditions to be studied are those that follow the extremely brief opening stage during which the voltage drops to a virtually constant value, E_2. At this moment the primary current, i_1, is equal to i_p at a voltage e_p; the secondary current, i_2, is equal to i_s. When L_1, L_2, C_1 and C_2 are the primary and secondary inductances and capacities (Fig. 1), and M the coefficient of mutual induction, the circuit equations are:

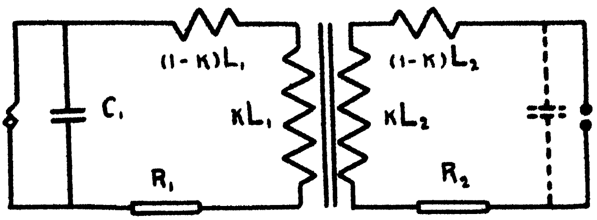

FIG. 1. *Circuit of induction coil.*

$$L_1\frac{d^2q_1}{dt^2} + M_2\frac{d^2q_2}{dt^2} + R_1\frac{dq_1}{dt} + \frac{q_1}{C_1} = 0$$

$$L_2\frac{d^2q_2}{dt^2} + M_1\frac{d^2q_1}{dt^2} + R_2\frac{dq_2}{dt} + E_2\left(\frac{dq_2}{dt}\right) = 0.$$

Providing that the potential across the spark, in the general case a function of the current $i_2 = dq_2/dt$, is virtually constant, the equations may be written in the form.

$$(L_1D^2 + R_1D + 1/C_1)q_1 + MD^2q_2 = 0$$
$$(L_2D^2 + R_2D)q_2 + MD^2q_1 + E = 0.$$

Eliminating q_1 and putting $M^2 = \kappa^2L_1L_2$, an equation for q_2 is obtained:

$$\left(D^4(1 - \kappa^2) + \left(\frac{R_1}{L_1} + \frac{R_2}{L_2}\right)D^3 + \left(\frac{R_1R_2}{L_1L_2} + \frac{1}{C_1L_1}\right)D^2 + \frac{R_2D}{L_1C_1}\right)q_2 = -\frac{E_2}{C_1L_1L_2},$$

or writing α_1 for R_1/L_1 and ω_1^2 for $1/L_1C_1$,

$$D\left(D^3 + \frac{\alpha_1 + \alpha_2}{1 - \kappa^2}D^2 + \frac{\omega_1^2 + \alpha_1\alpha_2}{1 - \kappa^2}D + \frac{\alpha_2\omega_1^2}{1-\kappa^2}\right)q_2 = -\frac{E_2\omega_1^2}{L_2(1 - \kappa^2)}$$

or

$$\left(D^3 + \frac{\alpha_1 + \alpha_2}{1 - \kappa^2}D^2 + \frac{\omega_1^2 + \alpha_1\alpha_2}{1 - \kappa^2}D + \frac{\alpha_2\omega_1^2}{1 - \kappa^2}\right)i_2 = \frac{-E_2\omega_1^2}{L_2(1 - \kappa^2)}.$$

Except when R_2 vanishes, the solution of this equation can be obtained in the usual way from the formula

$$q_2 = \int\epsilon^{m_3t}dt\int\epsilon^{(m_2-m_3)t}dt\int\epsilon^{(m_1-m_2)t}dt\int\frac{-E_2}{R_2}\epsilon^{m_1t}dt,$$

as

$$q_2 = A_1\epsilon^{m_1t} + A_2\epsilon^{m_2t} + A_3\epsilon^{m_3t} + A_4 - \frac{E_2}{R_2}t,$$

where 0, m_1, m_2 and m_3 are the solutions of the equation, with D considered as the unknown and E_2 equal to zero.

Elimination of q_2 from the differential equations leads to the same relation for q_1, but with the right-hand side equal to zero, so that

$$q_1 = B_1\epsilon^{m_1t} + B_2\epsilon^{m_2t} + B_3\epsilon^{m_3t} + B_4.$$

Hence, in that stage of the discharge in which the voltage at the electrodes remains virtually at the value E_2, the primary and secondary current, i_1 and i_2, are given by

$$i_1 = m_1 B_1 \epsilon^{m_1 t} + m_2 B_2 \epsilon^{m_2 t} + m_3 B_3 \epsilon^{m_3 t}$$

$$i_2 = m_1 A_1 \epsilon^{m_1 t} + m_2 A_2 \epsilon^{m_2 t} + m_3 A_3 \epsilon^{m_3 t} - \frac{E_2}{R_2} .$$

The seven constants of integration are determined from the conditions existing at the beginning of the second stage of the spark, while the values of m are given by the solutions of the equation

$$m^3 + \frac{\alpha_1 + \alpha_2}{1 - \kappa^2} m^2 + \frac{\omega_1^2 + \alpha_1 \alpha_2}{1 - \kappa^2} m + \frac{\alpha_2 \omega_1^2}{1 - \kappa^2} = 0,$$

or

$$m^3 + am^2 + bm + c = 0,$$

an equation that has at least one real root with a sign opposite to that of its last term. The character of the solution depends on the values of p, q and q^2/p^3, where

$$p = \frac{1}{9}\left(\left(\frac{\alpha_1 + \alpha_2}{1 - \kappa^2}\right)^2 - 3\,\frac{\omega_1^2 + \alpha_1\alpha_2}{1 - \kappa^2}\right) = \frac{1}{9}(a^2 - 3b)$$

$$q = \frac{1}{54}\left(9\,\frac{\alpha_1 + \alpha_2}{1 - \kappa^2}\,\frac{\omega_1^2 + \alpha_1\alpha_2}{1 - \kappa^2} - 2\left(\frac{\alpha_1 + \alpha_2}{1 - \kappa^2}\right)^3 - 27\,\frac{\alpha_2\,\omega_1^2}{1 - \kappa^2}\right) = \frac{1}{54}(9\,ab - 2a^3 - 27c).$$

In building ignition coils, α_1 and α_2 are kept small, at least, less than about 500, whereas $\omega_1^2 = 1/L_1C_1$ is very large, usually greater than 10^8. The coupling between primary and secondary is such that $\kappa \gtrsim 0.95$, or $\kappa^2 = M/L_1L_2$, about 0.9. Under these conditions p is negative and nearly equal to $-\omega_1^2/3(1 - \kappa^2) = -\omega^2/3$. Whenever p is negative

$$m_1 = -\sqrt{-p}\sinh\frac{u}{3} - \frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)} + i\sqrt{-3p}\cosh\frac{u}{3} = \mu + i\omega$$

$$m_2 = -\sqrt{-p}\sinh\frac{u}{3} - \frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)} - i\sqrt{-3p}\cosh\frac{u}{3} = \mu - i\omega$$

$$m_3 = 2\sqrt{-p}\sinh\frac{u}{3} - \frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)}$$

$$\sqrt{-p^3} = \sinh u.$$

A negative root and two complex roots, the latter corresponding to electrical oscillations, are obtained. Since in the expression for q the first term tends to be largest,

$$\frac{q}{\sqrt{-p^3}} \doteq \frac{\sqrt{3}}{2}\,\frac{\alpha_1 + \alpha_2}{\omega(1 - \kappa^2)} = \sinh u < 1;$$

when ω_1 is very high, $\sinh u$ becomes quite small, and for coils of moderate size the relations

$$m_1 = -\frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)} + i\omega = m_3 + i\sqrt{-3p}$$

$$m_2 = -\frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)} - i\omega = m_3 - i\sqrt{-3p},$$

hold for most practical purposes;

as though these roots were simply the solutions of a quadratic differential equation, namely of

$$(D^2 - 2m_2D + (m_2^2 + \omega^2))i_2 = 0.$$

The third root becomes

$$m_3 = -\frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)} = -\frac{a}{3}.$$

The angular frequency ω is given by $\sqrt{-3p}$, or

$$\omega = \frac{\omega_1}{\sqrt{1 - \kappa^2}},$$

as in ordinary tuned and coupled circuits. This formula is in good agreement with the experimental values. For a coil having $L_1 = 0.005$ *h.* and $C_1 = 0.46$ *μf.*, $\kappa = 0.95$, $L_2 = 11.6$ *h.*, the computed frequency is 10,640 cycles per sec., the measured frequency 10,750 (Finch). For a coil with $L_1 = 0.02$ *h.*, $C_1 = 0.041$ *μf.*, $\kappa = 0.97$, the corresponding frequency is 22,300 cycles per sec.

In the second stage of the discharge the current is therefore in general oscillating despite the constant voltage E_2. Its complete equation is

$$i_2 = m_3A_3\epsilon^{m_3t} - \frac{E_2}{R_2} + m_1A_1\epsilon^{(\mu+i\omega)t} + m_2A_2\epsilon^{(\mu-i\omega t)}$$

or

$$i_2 = m_3A_3\epsilon^{m_3t} - \frac{E_2}{R_2} + \epsilon^{\mu t}\Big((m_1A_1 + m_2A_2)\cos\omega t + i(m_1A_1 - m_2A_2)\sin\omega t\Big)$$

$$i_1 = m_3B_3\epsilon^{m_3t} - \frac{E_2}{R_2} + \epsilon^{\mu t}\Big((m_1B_1 + m_2B_2)\cos\omega t + i(m_1B_1 - m_2B_2)\sin\omega t\Big).$$

The constants A and B are obtained, first by computing q_1 and q_2 for $t = 0$, at which time $q_1 = C_1e_p$ and $q_2 = 0$, or C_2 virtually discharged, and second, by substituting the expressions obtained for q in the two differential equations determining q_2. This leads to the following seven equations for the seven unknowns, with $n = M/L_2$

$$\begin{array}{lllllll}
A_1 + & A_2 + & A_3 + A_4 & & & & = 0\\
 & & & B_1 + & B_2 + & B_3 & - C_1e_p = 0\\
 & & & m_1B_1 + & m_2B_2 + & m_3B_3 & - i_p = 0\\
m_1A_1 + & m_2A_2 + & m_3A_3 & & & & -\frac{E_2}{R_2} - i_s = 0\\
(m_1 + \alpha_2)A_1 & & & + m_1nB_1 & & & = 0\\
 & (m_2 + \alpha_2)A_2 & & & + m_2nB_2 & & = 0\\
 & & (m_3 + \alpha_2)A_3 & & & + m_3nB_3 & = 0
\end{array}$$

The system has the following exact solutions, in which (E) stands for $\left(\frac{E_2}{R_2} + i_s'\right)$:

$$A_1 = (m_2 - m_3)\frac{\alpha_2\omega^2nC_1e_p + ni_p\Big(m_1(m_2 + m_3) - \omega^2\Big) + (E)\Big(m_1\alpha_2 + m_1(m_2 + m_3) - \omega^2\Big)}{\alpha_2\Big(m_1m_2(m_2 - m_1) + m_3m_1(m_1 - m_3) + m_3m_2(m_2 - m_3)\Big)}$$

$$A_2 = (m_3 - m_1)\frac{\alpha_2\omega^2nC_1e_p + ni_p\Big(m_2(m_3 + m_1) - \omega^2\Big) + (E)\Big(m_2\alpha_2 + m_2(m_3 + m_1) - \omega^2\Big)}{\alpha_2\Big(m_1m_2(m_2 - m_1) + m_3m_1(m_1 - m_3) + m_3m_2(m_2 - m_3)\Big)}.$$

A similar expression is obtained for A_3 by cyclic increases in the subscripts of the m's. Moreover,

$$A_4 = \frac{n}{\alpha_2} i_p + \frac{1}{\alpha_2}\left(\frac{E_2}{R_2} + i_s\right) = \frac{M}{R_2} i_p + \frac{L_2}{R_2}\left(\frac{E_2}{R_2} + i_s\right)$$

while

$$\begin{aligned} B_1 &= -A_1 \frac{m_1 + \alpha_2}{m_1 n} \\ B_2 &= -A_2 \frac{m_2 + \alpha_2}{m_2 n} \\ B_3 &= -A_3 \frac{m_3 + \alpha_2}{m_3 n} . \end{aligned}$$

The solutions m_1, m_2 and m_3 being of the form

$$\begin{aligned} m_1 &= -s - \frac{a}{3} + i\omega = \mu + i\omega \\ m_2 &= -s - \frac{a}{3} - i\omega = \mu - i\omega \\ m_3 &= 2s - \frac{a}{3} , \end{aligned}$$

the denominator of the A's becomes equal to $2\alpha_2 i\omega(\omega^2 - d)$ or $2i\omega\alpha_2(\omega^2 + (\mu - m_3)^2)$. Grouping together the terms in ω^2 the expression for the aperiodic component of the current i_2 becomes

$$m_3 A_3 = \frac{m_3}{\alpha_2(\omega^2 + d)}\left(\alpha_2\omega^2 n C_1 e_p - n i_p \omega^2 - (E)\omega^2 + 2\mu m_3 n i_p + (E) m_3(\alpha_2 + 2\mu)\right) .$$

The sine wave forming part of i_2 is represented by $i(m_1 A_1 - m_2 A_2)$ sin ωt, its initial amplitude being therefore $i\mu(A_1 - A_2) - \omega(A_1 + A_2)$ or $i\mu Im(A_1 - A_2) - \omega Re(A_1 + A_2)$, where Im and Re are the imaginary and the real part of the expressions which follow them.

$$\begin{aligned} i(m_1 A_1 - m_2 A_2) = {} & \frac{\alpha_2 n C_1 e_p}{\alpha_2(\omega^2 + d)}\, \omega\left(\omega^2 + \mu(\mu - m_3)\right) \\ & + \frac{n i_p + (E)}{\omega\alpha_2(\omega^2 + d)}\left(\omega^2(m_3^2 + \mu^2 + m_3\mu) + \mu^2(m_3^2 - \mu^2)\right) \\ & + \frac{(E)\alpha_2}{\alpha_2\omega(\omega^2 + d)}\left(\omega^2(\mu + m_3) + \mu^2(\mu - m_3)\right) . \end{aligned}$$

The amplitude of the cosine wave becomes in the same way

$$\begin{aligned} & \mu Re(A_1 + A_2) + i\omega Im(A_1 - A_2) = (m_1 A_1 + m_2 A_2) \\ & = -m_3 \frac{\alpha_2 n C_1 e_p \omega^2}{\alpha_2(\omega^2 + d)} + m_3 \frac{(E) + n i_p}{\alpha_2(\omega^2 + d)}(\omega^2 - 2\mu m_3) + \frac{(E)}{\omega^2 + d}(\omega^2 + \mu^2 - 2\mu m_3) . \end{aligned}$$

These are the exact amplitudes.

With the much simpler expressions that in many practical applications are valid for m, namely, $s = 0$ and

$$\begin{aligned} m_1 &= \mu + i\omega = -\frac{a}{3} + i\omega \\ m_2 &= \mu - i\omega = -\frac{a}{3} - i\omega \\ m_3 &= -\frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)} = -\frac{a}{3} = \mu, \end{aligned}$$

the denominator of the constants A becomes equal to $2i\omega\alpha_2\omega^2$, and moreover the real part of

$$m_1A_1 + m_2A_2 = m_3\frac{2m_3^2ni_p + (E)(2m_3^2 + \alpha_2m_3)}{-\alpha_2\omega^2} + \frac{(E)(m_3 + \alpha_2) + m_3ni_p - \alpha_2m_3nC_1e_p}{\alpha_2},$$

while

$$Im(m_1A_1 - m_2A_2) = i\,\frac{(E)(3m_3^2 + 2m_3\alpha_2) + 3m_3^2ni_p + \omega^2\alpha_2nC_1e_p}{\alpha_2\omega}$$

$$m_3A_3 = m_3\frac{2m_3^2ni_p + (E)m_3(2m_3 + \alpha_2)}{\alpha_2\omega^2} + m_3\frac{\alpha_2nC_1e_p - ni_p - (E)}{\alpha_2}.$$

Taking into account the fact that in this case ω is very large, the expression for the discharge current in the low voltage stage becomes

$$i_2 = \frac{a}{3}\,\epsilon^{-\frac{a}{3}t}\left(\frac{ni_p + E_2/R_2 + i_s}{\alpha_2} - nC_1e_p\right) - \frac{E_2}{R_2}$$

$$i_2 = -\frac{E_2}{R_2} + \frac{a}{3}\,\epsilon^{-\frac{a}{3}t}\left(\frac{ni_p + E_2/R_2 + i_s}{\alpha_2} - nC_1e_p\right)(1 - \cos\omega t)$$

$$+\,\epsilon^{-\frac{a}{3}t}\left(\frac{E_2}{R_2} + i_s\right)\cos\omega t + \epsilon^{-\frac{a}{3}t}\,\omega nC_1e_p\sin\omega t\,.$$

The terms involving C_1 are generally small compared to the others, and since

$$-\frac{m_3}{\alpha_2} = \frac{\frac{\alpha_1}{\alpha_2} + 1}{3(1 - \kappa^2)}$$

may become large when α_2 is kept small, the expression for i_2 reduces in practice approximately to

$$i_2 = -\frac{E_2}{R_2} + \frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)\alpha_2}\,\epsilon^{-\frac{a}{3}t}\left(\frac{M}{L_2}\,i_p + \frac{E_2}{R_2} + i_s\right)(1 - \cos\omega t)\,.$$

If the secondary is shorted ($E_2 = 0$), the current becomes

$$i_2 = \frac{\alpha_1 + \alpha_2}{3(1 - \kappa^2)\alpha_2}\,\epsilon^{-\frac{a}{3}}\left(\frac{M}{L_2}\,i_p + i_s\right)(1 - \cos\omega t)\,.$$

Hence, in agreement with the experiment, in the region of constant voltage across the secondary, the discharge current consists in the simplest case of an exponentially decreasing electrical oscillation of audible frequency ω superimposed upon an aperiodic component that decreases according to the same law. The sum of the two components keeps the same sign. The current vanishes finally at the time t_f for which

$$\frac{1 + \alpha_1/\alpha_2}{3(1 - \kappa^2)}\,\epsilon^{-\frac{a}{3}t_f}\left(\frac{Mi_p}{L_2} + \frac{E_2}{R_2} + i_s\right) = E_2/R_2\,.$$

When E_2/R_2 is fairly large and the decay so rapid that $-at_f/3$ is smaller than unity,

$$t_f = \frac{3(1 - \kappa^2)}{\alpha_1 + \alpha_2},$$

that is, the secondary current has even then a duration that is larger than that corresponding to the natural period, ω, of the transformer.

For larger coils the value of sinh $\frac{u}{3}$ is not necessarily negligible, but follows roughly from the relation

$$4 \sinh^3 \frac{\mu}{3} + 3 \sinh \frac{\mu}{3} = \sinh \mu$$

as

$$-2 \sinh \frac{\mu}{3} = \sqrt[3]{-\sinh \mu + \sqrt{1 + \sinh^2 \mu}} + \sqrt[3]{-\sinh \mu - \sqrt{1 + \sinh^2 \mu}}$$

or

$$\sinh \frac{u}{3} \div \sinh \frac{u}{3} \cdot$$

Therefore

$$\begin{aligned} m_1 &= \frac{\alpha_2}{2} - \frac{\alpha_1 + \alpha_2}{2(1 - \kappa_2)} + i\omega \div -\frac{\alpha_1 + \alpha_2}{2(1 - \kappa_2)} + i\omega \\ m_2 &= \frac{\alpha_2}{2} - \frac{\alpha_1 + \alpha_2}{2(1 - \kappa^2)} - i\omega \div -\frac{\alpha_1 + \alpha_2}{2(1 - \kappa^2)} - i\omega \\ m_3 &= -\alpha_2. \end{aligned}$$

In this case the decay of the aperiodic component can be slowed down at will by keeping $\alpha_2 = R_2/L_2$ sufficiently small. Since $1 - \kappa^2$ is small, the oscillations will have died out long before the aperiodic portion of the current has decreased a great deal. Taking into account the fact that ω^2 is quite large and C_1 very small, the current is obtained by putting in the general formulas $\mu = -a/2$ and $m_3 = -\alpha_2$:

$$i_2 = -\frac{E_2}{R_2} + \left(\frac{Mi_p}{L_2} + \frac{E_2}{R_2}\right)\left(\epsilon^{-\alpha_2 t} - \epsilon^{\left(\frac{\alpha_2}{2} - \frac{\alpha_1 + \alpha_2}{2(1 - \kappa^2)}\right)t} \cos \omega t\right).$$

With $i_0 = Mi_p/L_2$ as its initial strength, the aperiodic component is the same as it would be were a current i_0 set up and allowed to decay in the secondary in the absence of the primary windings; such a current corresponds to the complete sharing of the magnetic flux by the primary and the secondary:

$$Mi_p = L_2 i_0.$$

In the later stage of the discharge the current becomes simply

$$i_2 = -\frac{E_2}{R_2} + \left(i_0 + \frac{E_2}{R_2}\right)\epsilon^{-\frac{R_2}{L_2}t}.$$

and the time required for the current to drop from i_0 to i_2 is

$$t = \frac{L_2}{R_2} \ln \frac{i_0 R_2 + E_2}{i_2 R_2 + E_2}.$$

This duration determines the extent to which the coil is discharged.

For large coils this formula is in agreement with observation (McFarlane).

In dealing with the course which the aperiodic component takes, the constants of only the secondary windings need be considered, the circuit equations reducing to

$$\frac{di_2}{dt} + \frac{R_2}{L_2} i_2 + \frac{E_2}{L_2} = 0.$$

In view of the simple laws obeyed by E_2, for instance $E_2 = C - ci_2$, this equation is the same as that valid for ordinary discharge tube circuits, so that the glow may present all the types found at lower pressures (Kock).

For a small coil, the following constants may be used (Finch):

$L_1 = 0.005$ h.
$R_1 = 3$ ohms
$\alpha_1 = 600$
$L_2 = 11.6$ h.
$R_2 \doteq 300$ ohms
$\alpha_2 \doteq 26$

$a = 6.66$

$\kappa = 0.95$
$M = \kappa\sqrt{L_1L_2} = 0.229$
$n = M/L_2 = 0.02$ A. per A.
$1 - \kappa^2 = 0.0975$

$C_1 = 0.46\ \mu$f.
$\omega = 66{,}816$
$f = 10{,}640$
$nC_1e_p < 10^{-7}$
$C_2 = 10^{-10}$ f.
$E_2/R_2 \doteq 0.050$

$E_2 = 360\text{–}380$ v.
$i_p = 2$ A.
$e_p < 5$ v.

and therefore,

$$i_2 = 0.22\,\epsilon^{-6\ 66t}\,(1 - \cos 66{,}816t)$$

For a large coil the following constants are appropriate (McFarlane):

$L_1 = 0\ 1$ h.
$R_1 = 39$ ohms
$\alpha_1 = 400$
$L_2 = 1500$ h.
$R_2 = 28{,}000$ ohms
$\alpha_2 = 19$

$$a = \frac{\alpha_1 + \alpha_2}{1 - \kappa^2} = 158$$

$\kappa = 0\ 94$
$M = 11\ 2$
$n = M/L_2 = 0.0075$
$1 - \kappa^2 = 0.12$

$C_1 = 2.67\ \mu$f.
$\omega = 5600$
$C_2 = 10^{-10}$ f.

$E_2 = 380$ v.
$i_p = 2$ A.
$e_p = 12$ v.

$E_2/R_2 = 0.014$

and therefore,

$$i_2 = -\frac{E_2}{R_2} + \left(\frac{Mi_p}{L_2} + \frac{E_2}{R_2}\right)\left(\epsilon^{-\alpha_2 t} - \epsilon^{\left(\alpha_2 - \frac{\alpha_1+\alpha_2}{1-\kappa^2}\right)\frac{t}{2}}\cos\omega t\right)$$

$$= -0.013 - 0.028\,\epsilon^{-1760t}\cos\omega t + 0.028\,\epsilon^{-19t}.$$

Curve of Sloping Voltage against Current

So long as the electrodes are separated by a gap barely allowing the negative glow to develop, which involves a distance of about 0.008 mm. at atmospheric pressure, the drop of potential reduces to the normal cathode fall, about 375 volts in air between copper discs and 277 volts between zinc plates, regardless of the pressure. When the distance is increased, the potential gradient across the positive column must be added. This gradient increases with increasing pressure p, measuring about $0.3\,p$ volts per mm. in nitrogen and four times this amount in oxygen, when the pressure is measured in millimetres of mercury. Lower currents require a higher gradient, usually represented by $g + h/i$, where h is not far from unity. The voltage across the spark is therefore

$$E_2 = c + l\,(g + h/i)\,.$$

In air, C is about 380 volts for copper electrodes, g equal to 108 and $h = 0.8$ (McFarlane). The curvature introduced by the term h/i in the curve of voltage against current is so small as a rule that over wide ranges of current the voltage may be represented by a straight line.

The only change that a slightly sloping, or rising, but straight curve of voltage against current causes in the mathematical equations of the problem is the addition of $\mp\alpha_3$ to all the terms containing α_2. In view of the small currents involved, less than 50 ma., and the rather large values of L_2, the existence of the slope $\mp R_3$ in the characteristic curve, beginning in sparks at about 500 volts and several milliamperes current, would probably not be revealed by ordinary measurements with the cathode ray tube even if $-\alpha_3 = R_3/L_2$ were as large as 500 or 600. When appreciable capacity is present in parallel with the gap, however, it absorbs a current, i_c, given by

$$i_c - i_2 = C_2 dE_2/dt = \pm C_2 R_3 .$$

The case where $-\alpha_3$ just neutralizes α_2 deserves special mention. Under these conditions, most favorable to an experimental study, the ignition coil behaves as if there were no resistance in the secondary, whereas, in practice, R_2 cannot be neglected, not at least if, as is sometimes the case, a resistance of several thousand ohms is included in order to record the current changes with the cathode ray. When $(\alpha_2 - \alpha_3)$ vanishes, as seems sometimes to be the case, the differential equation reduces to a quadratic relation.

$$D^2\left(D^2 + \frac{\alpha_1}{1-\kappa^2} D + \frac{\omega_1^2}{1-\kappa^2}\right)q_2 = -\frac{\omega_1}{(1-\kappa^2)L_2} E_2 .$$

The frequency of oscillation is the same as before; the damping has been decreased, and the current is given by the simple formula

$$i_2 = \frac{M}{L_2} i_p(1 - \epsilon^{-\frac{a}{2}t} \cos \omega t) + i_s \epsilon^{-\frac{a}{2}t} - \frac{E_2}{L_2} t ,$$

where

$$a = R_1/L_1(1 - \kappa^2)$$

and

$$M/L_2 = \kappa\sqrt{L_1/L_2} .$$

The current consists of a damped oscillation about the straight line $(Mi_p - E_2 t)/L_2$. Once the oscillations have vanished, the secondary current continues to decay to zero along the time axis, giving a total duration of this second, and by far the longest, stage of the spark of

$$t_f = Mi_p/E_2 \text{ sec.}$$

It lasts at least a few milliseconds, whereas the breakdown proper takes less than a microsecond (McFarlane, Finch).

With a slightly more negative value of $-\alpha_3$ a stage is reached where the sum $(\alpha_1 + \alpha_2 - \alpha_3)$ disappears. This change again scarcely affects the frequency which remains at the value given by $\omega_1/\sqrt{1 - \kappa^2}$, but it removes all damping. The equation for the current is

$$\left(D^3 - \omega^2 D - (\alpha_3 - \alpha_2)\omega^2\right)i_2 = E_2\omega^2/L_2$$

with the solutions, since

$$\frac{(\alpha_3 - \alpha_2)\omega_1^2}{2(1-\kappa^2)} \ll \sqrt{\frac{\omega_1^6}{27(1-\kappa^2)^3}} ,$$

$$m_{1 \text{ or } 2} = \pm i \frac{\omega_1}{\sqrt{1-\kappa^2}} , \qquad m_3 = 0,$$

solutions which might have been obtained directly from the previous simplified quadratic equation for m_3 and ω. They correspond to oscillations of constant amplitude

$$i_2 = \left(\frac{E}{R_2} + i_e\right)\cos\omega t - \frac{E_2}{R_2} - \frac{M}{L_2} C_1 e_p \sin\omega t\,,$$

where the last term is most often negligible.

Beyond this point the discharge enters the stage where the amplitudes instead of being damped increase with each period and finally, owing to the rapidly increasing cathode drop, the oscillations degenerate into slow relaxation currents. At the same time, for large fluctuations in the current, the value of M is no longer constant.

The Aperiodic Discharge

When, on the other hand, as a result of the introduction of a large condenser in the primary, or a large resistance in the secondary, circuit, the value of $R_2/\omega_1 L_2$ increases, the sign of p changes from negative to positive, so that

$$p > 0 \qquad q > 0 \qquad q^2 > p^3 \qquad \cosh u = \frac{+q}{\sqrt{p^3}}\,.$$

The solutions m_1, m_2 and m_3 now depend on

$$\begin{aligned}
m_1 &= -\sqrt{p}\cosh\frac{u}{3} - \frac{a}{3} + i\sqrt{3p}\sinh\frac{u}{3} &&= \mu + i\omega \\
m_2 &= -\sqrt{p}\cosh\frac{u}{3} - \frac{a}{3} - i\sqrt{3p}\sinh\frac{u}{3} &&= \mu - i\omega \\
m_3 &= +2\sqrt{p}\cosh\frac{u}{3} - \frac{a}{3} &&= -2\mu + \frac{a}{3}\,,
\end{aligned}$$

where p and q are conveniently written as

$$p = \frac{\omega_1^2}{9}\left(\left(\frac{\alpha_1 + \alpha_2}{\omega_1(1 - \kappa^2)}\right)^2 - 3\,\frac{1 + \dfrac{\alpha_1\alpha_2}{\omega_1^2}}{1 - \kappa^2}\right)$$

$$q = \frac{\omega_1^3}{54}\left(\frac{9}{\omega_1}\,\frac{\alpha_1 + \alpha_2}{1 - \kappa^2}\,\frac{1 + \dfrac{\alpha_1\alpha_2}{\omega_1^2}}{1 - \kappa^2} - \frac{2}{\omega^3_1}\left(\frac{\alpha_1 + \alpha_2}{1 - \kappa^2}\right)^3 - \frac{27}{\omega_1}\,\frac{\alpha_2}{1 - \kappa^2}\right),$$

in order to illustrate the importance of the factor $\alpha_2/\omega_1(1 - \kappa^2)$. When α_1 is small, the expression for p changes from negative to positive near the frequency for which

$$\frac{\alpha_1 + \alpha_2}{\sqrt{3}(1 - \kappa^2)} \geqslant \omega_1$$

whilst, q keeps its sign. For $\kappa = 0.95$ the equation becomes, for small α_1's, $\alpha_2 = 0.55\omega_1$; for $\kappa = 0.98$ it is $\alpha_2 = 0.35\,\omega_1$.

As α_2 increases, the natural frequency of oscillation given by $\omega \doteq \sqrt{3p}$ $\sinh\frac{u}{3}$ decreases (Table I). The last simple form the discharge may assume is the aperiodic stage, which is obtained when $p > 0$, but $q^2 \leqslant p^3$, or

$$0 < \frac{q^2}{p^3} < 1\,.$$

This condition is satisfied when $(\alpha_1 + \alpha_2)$ is rather large, the coupling tight $(\kappa > 0.95)$, and when q is nearly zero or negative. By starting with a coil having a small value of α_1 and a large ratio $R_2/L_2 = \alpha_2$, the values of α_2 and κ may always be so chosen that q becomes slightly smaller than the square root of p^3. In this case, which may obtain over a portion only, or over the entire duration of the discharge'

$$\cos u = \frac{q}{\sqrt{p^3}}$$

$$m_1 = -\sqrt{p}\cos\frac{u}{3} - \frac{a}{3} + \sqrt{3p}\sin\frac{u}{3}$$

$$m_2 = -\sqrt{p}\cos\frac{u}{3} - \frac{a}{3} - \sqrt{3p}\sin\frac{u}{3}$$

$$m_3 = 2\sqrt{p}\cos\frac{u}{3} - \frac{a}{3}$$

TABLE I

INFLUENCE OF INCREASING RESISTANCE IN THE SECONDARY UPON THE ANGULAR FREQUENCY OF OSCILLATION, $\omega = \sqrt{3p}\sinh u/3$

$\alpha_1 \doteq 0$; $\omega_1 = 2000$; $1-\kappa^2 = 0.04$

α_2	p/ω_1^2	$\sqrt{p}/\omega_1$	$\sqrt{p^3}/\omega_1^3$	q/ω_1^3	$\cosh u$	$\cosh\frac{u}{3}$	$\sinh\frac{u}{3}$	$\sqrt{3p}$	$\frac{a}{i}$
Oscillating stage									
690	<0								
695	0.052	0.228	0 0118	7.63	647	5.56	5 46	790	1917
700	0.118	0.344	0.045	7.28	162	3.48	3 34	1190	1944
750	1.423	1.19	1.7	4	2.4	1.13	0 52	2846	2083
Aperiodic stage									
				0		1	0		
800	2.777	1.667	4.6	−0 37	−0.08	0.82	0.57	2886	2222
900	5.73	2.394	13.7	−11.5	−0.83	0 62	0.79	4147	2500
1000	9.03	3.005	27	−26.5	−0.98	0.55	0 83	5206	2777
∞	a^2/ω_1^2	a/ω_1		a^3/ω_1^3	−1	0.5	0.87		

In the aperiodic stage the ordinary trigonometric functions take the place of sinh and cosh. At the limit the current reduces to

$$i_2 = \left(\frac{E_2}{R_2} + i_s\right)\epsilon^{-\frac{\alpha_1+\alpha_2}{1-\kappa^2}t} - \frac{E_2}{R_2}\,.$$

The current decreases according to an exponential law until the energy is exhausted (10).

Intermittent Discharges

So far, the discharge has been treated as if any current between 0 and 100 ma. could pass at the constant or nearly constant voltage obtained between the electrodes. In reality, for a discharge to be maintained at the glow voltage the current must exceed a certain smallest value, a few milliamperes in the case of short gaps 1 or 2 mm. wide. If in its variations the current enters a region where this condition is not fulfilled, the discharge is likely to stop without necessarily having discharged the coil. Provided, however, that the coil is able to recharge the electrodes in the interval without current, the discharge may restart at or near the spark potential, or even near the glow voltage in those cases where the path which the current has followed remains fairly conducting. In this case the current increases suddenly from zero to a high value, only to decrease again, and this cycle is repeated until the energy in the coil has been dissipated. When $R_2 > L_2$ and the aperiodic component of the current, the component which merely depends on the constants of the secondary, disappears at a voltage E_0, which is lower than the starting voltage E_1, and E is the potential which the coil is capable of generating in the absence of a discharge, then as in the case of the flashing neon tubes, the period at which the discharges follow one another is (Schallreuter)

$$t = R_2C_2 ln \frac{E - E_0}{E - E_1} + C_2R ln \frac{E_1}{E_0},$$

where the last term refers to the duration of the discharge. The difference between E_0 and E_1 depends on the shape and distance of the electrodes, and for the same value of E_0 and E_1 the ratio $(E - E_0)/(E - E_1)$ is smaller, or more nearly equal to unity, the higher E. With discharge tubes, a value of 2 or 3 is often obtained for this ratio. With these figures and C_2, the capacity associated with the gap, equal to $100 \times 10^{-12} f.$, R_2 a few thousand ohms, the frequency becomes of the order of 1000 kc., so that it falls in the middle of the broadcast band.

When L_2 is large, the duration of the discharge is increased to such an extent that it may determine the frequency of the intermittence. Instead of rapidly increasing with increasing voltage or primary current, the frequency tends toward a constant value

$$f = \frac{1}{2\pi\sqrt{L_2C_2}},$$

which, in view of the small value of C_2, may still lie in the region of high pitched sound waves (Kock).

A particular case of these recurrent discharges presents itself when the primary current is just barely sufficient to break down the gap without being able to establish a fully developed glow discharge. Under these conditions the discharge starts repeatedly at the sparking voltage, and several sparks follow in rapid succession. A large capacity in parallel with the gap favors this type of multiple spark, the so-called condensed spark (4).

The existence of intermittent or recurrent discharges has been well demonstrated under operating conditions (9). The interval between two flashes varies from one spark to the next one, and even within the same group of partial discharges, between 1 and 30 microseconds, corresponding to the periods of waves of 300–3000 metres. At each cycle the wires leading from the coil to the spark gap are excited to resonance, so that reception of short waves is interfered with at the same time.

Prevention of Oscillations

In the case of internal combustion engines, the oscillations of the various kinds described do not seem to improve the performance of the gap, so far as ignition is concerned, since the firing of the charge, requiring merely a temperature of about 700° C. at some point in the mixture, is well under way when the low voltage stage sets in. The oscillations are, however, liable to produce noises and disturbances in the reception of radio waves.

Since the initial strength of the low voltage stage of the discharge current is nearly directly proportional to the primary current at break, it can be readily weakened by lowering the primary current, but such a reduction is likely to create multiple sparks. A more direct procedure for preventing oscillations, though difficult to apply in practice, is to close the primary circuit as soon as breakdown has occurred. The spark is rapidly extinguished. Grid-controlled discharge tubes would be suitable for this purpose.

There still remains in any case the disturbance created by the spark proper, or the surge traveling along the leads owing to the sudden drop in potential at the moment of the breakdown. Its duration, less than a microsecond, is about the same as the natural period of the lead wires acting as half-wave antennas. Strong oscillations are therefore set up at each passage of the spark. The inductance of two straight parallel wires of radius r cm. spaced a cm. apart is $0.4\ ln\ (a/r)$ microhenry per metre, or about 0.28 μh. per metre for wires touching each other, and the capacity is 10^{-10} farads per metre, equal to $1.06/ln(a/r)$, or $0.15 \times 10^{-10}\ f.$ per metre for wires in contact, so that the angular resonance frequency of the wires connecting coil and spark,

$$\omega_2^2 = \frac{1}{L_2 C_2} - \frac{R_2^2}{4L_2^2},$$

is seen to correspond to waves of less than 40 metres, provided that R_2 is small. This circuit can be rendered aperiodic by increasing R_2 and by decreasing the value of L_2 to that for a single straight wire.

The usual remedy is to insert resistance in the secondary until the noise vanishes. Tests on a wide variety of motors, ranging in output from 1 to 60 hp., have shown that resistances of 5,000-15,000 ohms, preferably wire-wound, long and with little self-inductance, greatly weaken the noises without reducing measurably the power of the engine (5).

The formula for ω_2 shows that the lower the value of L_2 the easier it is to suppress the oscillations, and that, as experience shows, it cannot be accomplished by inserting choke-coils between spark and secondary. The same statement applies to incomplete screening of the spark circuit, which is likely to increase L_2 and to add capacitance. Condensers and filters merely shift the resonance frequency to a different wave band.

It is more difficult to deal with the intermittent discharge. Its strength depends on the difference between starting and stopping voltage. The difference increases, in general, with increasing pressure and decreasing capacitance of the electrodes. It would be of general interest to study spark discharges from this point of view in the same detail in which discharges at low pressures have been investigated.

Multiple sparks, finally, are avoided when the current at break in the primary is made strong enough to produce more than the lowest breakdown voltage in the secondary.

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SOME CALCULATIONS OF FIELD STRENGTH DISTRIBUTION IN THE VERTICAL PLANE OF DOUBLE-TAPERED MASTS[1]

By K. A. MacKinnon[2]

Abstract

The approximate current distribution with height in vertical tower antennae of non-uniform cross section is calculated by assuming that the cross section is that of a cylinder whose diameter changes discontinuously. The field strength distribution in the vertical plane is then calculated for this current distribution and compared with field measurements of Ballantine. This is repeated using the experimentally determined current distribution of Gihring and Brown which results in a much closer check with Ballantine's measurements.

The results were then used to calculate the field strength distribution in the vertical plane of an array comprising a 0 597λ vertical double-tapered tower as radiator, and a 0.250λ vertical tower of the self-supporting type as a fed reflector.

During some studies of adjacent channel interference from high powered broadcasting stations, a mathematical investigation was undertaken to ascertain the radiation characteristics of an array comprising a 0.597 wave vertical tower of the Blaw-Knox guyed cantilever type as radiator, and a quarter-wave vertical tower of the self-supporting type as reflector.

The radiating system thus presented has several features not usually encountered in arrays. In the first place, the towers comprising the array are of unequal heights (0.597λ and 0.25λ). In the second place, the non-uniform cross section of the towers results in a current distribution with height which, especially in the case of the higher tower, departs considerably from the sinusoidal distribution to be expected in a thin wire of uniform cross section.

Available Data

The published information on the dimensions and actual electrical performance of the guyed cantilever type of tower is very meagre. There is the recent paper by Ballantine (1), which shows the results of some measurements of the electric field distribution in the vertical plane about the WABC radiator of this type (see solid curve, Fig. 5). One observes the absence of any minimum in the neighborhood of 45° zenith angle, which minimum would be expected from a sinusoidal current distribution in the tower. A more recent paper by Gihring and Brown (2) gives the current distribution as measured on an experimental model of the guyed cantilever type of tower. This distribution is far from sinusoidal (compare Curves A and C in Fig. 3).

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Contribution from the Engineering Department, Canadian Radio Broadcasting Commission, Ottawa, Canada. This paper was presented at a joint meeting of the Institute of Radio Engineers and the American Section, U.R.S.I., at Washington, April 26, 1935.

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Note.—*While the author was preparing this manuscript, there appeared in the Proceedings of the Institute of Radio Engineers, a letter to the editor by Hans Roder (4) in which he derives the current distribution in this type of tower by treating it as a concentric transmission line.*

Theoretical Investigation of the Current Distribution

Typical cross sections parallel to the axis of the Blaw-Knox cantilever type towers are shown in Figs. 1 and 3. Although the cross section perpendicular to the axis is square it will be considered circular henceforth. Again, although the cross section perpendicular to the axis varies uniformly throughout its length, it will be considered as changing discontinuously as illustrated in the right-hand sketch of Fig. 3. The effect of such a discontinuity on the current distribution can be readily shown for the ideal case.

Let the discontinuity be revealed only as a change in the capacity and inductance per unit length. Assuming that the top section of length X_1 has capacity C_1 and inductance L_1 per unit length, the next section, C_2 and L_2 per unit length, then, according to the simple theory

$$-\frac{dv}{dx} = jL\omega i \qquad -\frac{di}{dx} = jC\omega v$$

which have the general solution

$$v = A\cos B(x+\theta) \qquad i = \frac{AB}{jL\omega}\sin B(x+\theta)$$

where A and θ are constants and $B = \sqrt{LC\omega^2}$. The boundary conditions are

$$\text{when} \quad x = 0, \quad i_1 = 0, \quad \therefore \theta_1 = 0 \tag{1}$$

$$\text{when} \quad x = \underline{\overline{X}}_1, \quad v_1 = v_2, \quad i_1 = i_2$$

Thus

$$A_1 \cos B_1\left(\underline{\overline{X}}_1\right) = A_2 \cos B_2\left(\underline{\overline{X}}_1 + \theta_2\right) \tag{2}$$

and

$$\frac{A_1B_1}{jL_1\omega}\sin B_1\left(\underline{\overline{X}}_1\right) = \frac{A_2B_2}{jL_2\omega}\sin B_2\left(\underline{\overline{X}}_1 + \theta_2\right) \tag{3}$$

Assuming that the velocity in each section is the same as that *in vacuo*

$$B_1 = B_2 = \frac{2\pi}{\lambda}$$

Dividing Equation (3) by Equation (2) the expression

$$\tan\frac{2\pi}{\lambda}\left(\underline{\overline{X}}_1 + \theta_2\right) = \frac{C_1}{C_2}\tan\frac{2\pi}{\lambda}\left(\underline{\overline{X}}_1\right) \tag{4}$$

is obtained.

An approximate relation between the radius of the section of the tower and its capacity per unit length is now necessary. Assume that r is the radius of any section of the tower. Let l be the total height of the tower. Assume constant density of charge (σ) over the surface of a tower of length $2l$ (to include image in earth) and radius r.

$$\text{Potential at any point } P = \frac{2\pi r\,dx\,\sigma}{\sqrt{r^2 + x^2}}$$

$$\text{Potential at midpoint} = 2\pi r\sigma \int_{-l}^{+l} \frac{dx}{\sqrt{r^2 + x^2}}$$

$$= 4\pi r\sigma \sinh^{-1}\frac{l}{r}$$

$$\text{Capacity} = \frac{\text{Charge}}{\text{Potential}} = \frac{2\pi r(2l)\sigma}{4\pi r\sigma \sinh^{-1} l}$$

Thus capacity per unit length

$$\frac{1}{\sinh^{-1}\frac{l}{r}} \tag{5}$$

Substituting Relation (5) in Equation (4) the expression

$$\tan\frac{2\pi}{\lambda}\left(\overline{X}_1 + \theta_2\right) = \frac{\sinh^{-1}\frac{l}{r_2}}{\sinh^{-1}\frac{l}{r_1}}\tan\frac{2\pi}{\lambda}\left(\overline{X}_1\right) \tag{6}$$

is obtained. As r_2 is greater than r_1, it is seen that θ_2 is negative if $\overline{X}_1$ is less than 90°. Thus, although the current distribution from $x = 0$ to $\overline{X}_1$ is sinusoidal, so that $i_{\overline{X}_1} = \sin\frac{2\pi}{\lambda}\left(\overline{X}_1\right)$, yet after the discontinuity the current varies as though at $\overline{X}_1$ the current had attained only the value $\sin\frac{2\pi}{\lambda}\left(\overline{X}_1 + \theta_2\right)$, where θ_2 is negative. Similarly at the next discontinuity, which occurs at $x = \overline{X}_1 + \overline{X}_2$, where r changes from r_2 to r_3

$$\tan\frac{2\pi}{\lambda}\left(\overline{X}_1 + \theta_2 + \overline{X}_2 + \theta_3\right) = \frac{\sinh^{-1}\frac{l}{r_3}}{\sinh^{-1}\frac{l}{r_2}}\tan\frac{2\pi}{\lambda}\left(\overline{X}_1 + \theta_2 + \overline{X}_2\right) .$$

Proceeding in this way an idea is obtained of the current distribution in a tower such as that illustrated in Fig. 1. The data in Table I were calculated by the above method.

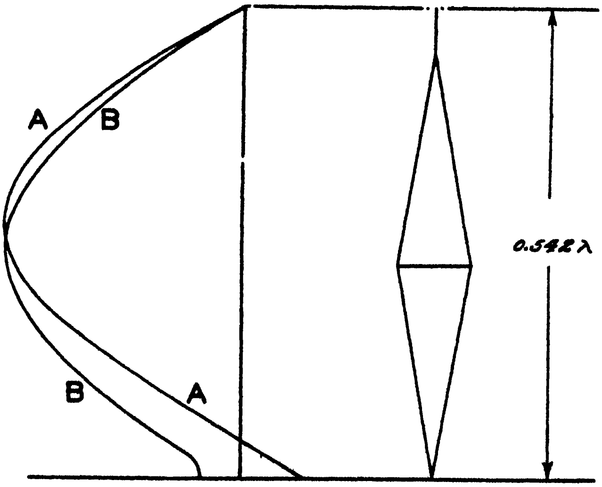


FIG. 1. *Current distribution in 0 542λ mast. A—Sinusoidal distribution. B—Distribution calculated by method presented herein.*

The data in the third and fourth columns are plotted in Fig. 1 as Curve A and Curve B respectively. Thus, Curve A is the current distribution to be expected on a wire of height 0.542λ, and Curve B is the current distribution calculated for the 0.542λ tower illustrated at the right side of Fig. 1.

TABLE I

Distance from top of tower as a fraction of the total height of the tower, x/h	Ratio of capacity, $\sinh^{-1}\frac{l}{r}$	Space angle, $\frac{360°}{\lambda}x$	Current angle, $\frac{360°}{\lambda}(x+\Sigma\theta_n)$	Distance from top of tower as a fraction of the total height of the tower, x/h	Ratio of capacity, $\sinh^{-1}\frac{l}{r}$	Space angle, $\frac{360°}{\lambda}x$	Current angle, $\frac{360°}{\lambda}(x+\Sigma\theta_n)$
0	8.29	0	0	0.55	3.43	107.20	94.05
0.05	5.52	9.75	9.75	0.65	3.69	126.80	113.85
0.15	4.71	29.30	26.08	0.75	4.20	146.20	131.68
0.25	4.20	48.80	42.13	0.85	4.89	165.80	147.60
0.35	3.86	68.30	58.40	0.95	7.27	185.50	162.23
0.45	3.60	87.70	75.53	1.00	—	195.00	164.55

Derivation of Field Strength Distribution

There will now be derived the general equation for the root mean square value of the field strength (E_θ) at a zenith angle (θ) to a vertical radiator having the current distribution ($I(x)$) at a given frequency $\left(\frac{c}{\lambda}\right)$, and situated on soil having a given conductivity (σ) and dielectric constant (ϵ).

Consider a vertical radiator with height l. The value of the current at height X from the ground is $I(x)$. At a remote point, P, on the radial through the antenna base making an angle θ with the zenith, the electric field due to the current in dx is (3)

$$de_1 = \frac{\sin\theta}{c^2 r_0} f''\left(t - \frac{r_0 - x\cos\theta}{c}\right)$$

where

$$f''(t) = \frac{\partial i}{\partial t}\,dx$$

or

$$de_1 = \frac{\sin\theta}{c^2 r_0}\left(I(x)\,dx\right)\frac{2\pi c}{\lambda}\cos\left[\frac{2\pi c}{\lambda}\left(t - \frac{r_0 - x\cos\theta}{c}\right)\right]$$

or

$$de_1 = \frac{2\pi}{c r_0 \lambda}\left[I(x)\,dx\sin\theta\cos\frac{2\pi c}{\lambda}\left(t - \frac{r_0 - x\cos\theta}{c}\right)\right]$$

Similarly the field due to the image of dx is

$$de_2 = \frac{2\pi R}{c r_0 \lambda}\left[I(x)\,dx\sin\theta\cos\frac{2\pi c}{\lambda}\left(t - \frac{r_0 + x\cos\theta}{c}\right)\right],$$

where R = reflection coefficient of the earth;

$$= \frac{\cos\theta(\epsilon - j2\sigma T) - \sqrt{\epsilon - \sin^2\theta - j2\sigma T}}{\cos\theta(\epsilon - j2\sigma T) + \sqrt{\epsilon - \sin^2\theta - j2\sigma T}}$$

where ϵ, σ are in *e.s.u.* and T = period.

Then the total field at P due to dx is

$$de = de_1 + de_2$$

$$de = \frac{2\pi}{c r_0 \lambda} I(x)\,dx\sin\theta\left[\cos\frac{2\pi c}{\lambda}\left(t - \frac{r_0 - x\cos\theta}{c}\right) + R\cos\frac{2\pi c}{\lambda}\left(t - \frac{r_0 + x\cos\theta}{c}\right)\right].$$

The bracketed term can be rearranged so that

$$\text{bracket} = (R+1)\cos\frac{2\pi}{\lambda}(ct-r_0)\cos\frac{2\pi}{\lambda}(x\cos\theta) + (R-1)\sin\frac{2\pi}{\lambda}(ct-r_0)\sin\frac{2\pi}{\lambda}(x\cos\theta).$$

Thus

$$E_\theta = \frac{2\pi}{cr_0\lambda}\sin\theta\left[\cos\frac{2\pi}{\lambda}(ct-r_0)\,.\,(R+1)\int_0^l I(x)\cos\frac{2\pi}{\lambda}(x\cos\theta)\,dx + \sin\frac{2\pi}{\lambda}(ct-r_0)\,.\,(R-1)\int_0^l I(x)\sin\frac{2\pi}{\lambda}(x\cos\theta)dx\right].$$

The root mean square value of E_θ is then

$$\underset{r.m.s.}{E_\theta} = \frac{\pi}{cr_0\lambda}\sin\theta\sqrt{\left[(R+1)\int_0^l I(x)\cos\frac{2\pi}{\lambda}(x\cos\theta)dx\right]^2 + \left[(R-1)\int_0^l I(x)\sin\frac{2\pi}{\lambda}(x\cos\theta)dx\right]^2}\,.$$

Field Strength Distribution for Calculated Current Distribution

For the case represented in Fig. 1 the current distribution can be represented approximately by

$$I(x) = \sin\frac{1\ 675\pi}{\lambda}(l-x).$$

Assuming New Jersey soil characteristics ($\sigma = 4 \times 10^{-14}\,e.m.u.$, $\epsilon\ 13 = e.s.u.$), a frequency of 860 kilocycles, and this $I(x)$, Curve C of Fig. 2 is obtained for E_θ.

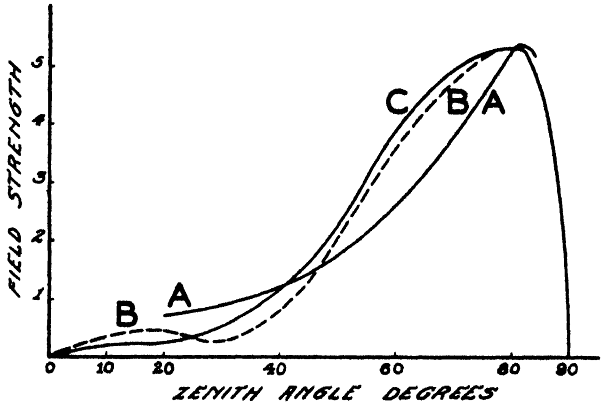


FIG. 2. *Field strength distribution in vertical plane of 0.542λ mast, over New Jersey soil. A—Ballantine's measurement of WABC (eastern side). (See Reference (1), p. 624, Fig. 41.) B—Calculated from sinusoidal distribution and for New Jersey soil. C—Calculated from distribution derived by method presented herein.*

Curve B of Fig. 2 is E_θ for New Jersey soil and a 0.542λ vertical wire, where, of course,

$$I(x) = \sin\frac{2\pi}{\lambda}(l-x).$$

Curve A, Fig. 2 is a graphical representation of Ballantine's measurement of E_θ on the eastern side of WABC (860 kilocycles, Wayne, New Jersey).

It is seen in Fig. 2 that although the calculated distribution (Curve C) has no minimum like the sinusoidal distribution (Curve B), yet it does not check satisfactorily with the experimental values (Curve A).

Field Distribution of Gihring and Brown's Current Distribution

Accordingly, the case of the 0.597λ mast for which there is Gihring and Brown's experimental distribution is next taken. Fig. 3 shows on the right-hand side the shape of the mast assumed for the calculations, and the actual shape. $I(x)$ is found for this mast by the method just outlined, and the current distribution is found to be as shown in Curve B, Fig. 3. Curve A gives the sinusoidal distribution, and Curve C, the experimentally measured distribution of Gihring and Brown.

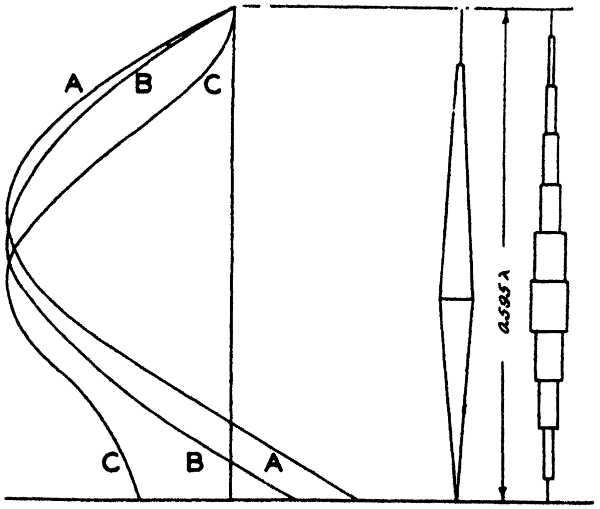


FIG. 3. *Current distribution in 0.597λ mast. A—Sinusoidal distribution. B—Distribution calculated by method presented herein. C—Distribution as experimentally measured by Gihring and Brown (2).*

The calculated distribution fails, as it always must, to indicate the very low current at the top of the mast.

To ascertain how the Gihring and Brown distribution checked with Ballantine's field measurements, an empirical relation was evolved for Curve C of Fig. 3. This is

$$I(x) = \frac{I_{\text{Loop}}}{2}\left[1 + \sin\frac{2\pi}{\lambda_0}\left(x - \frac{\lambda_0}{10}\right)\right],$$

where $\lambda_0 = 0.716\lambda$.

A comparison of this $I(x)$ and the experimental curve it represents is given in Fig. 4. The solid curve, B, is Gihring and Brown's values, whilst the dotted curve, C, is $I(x)$.

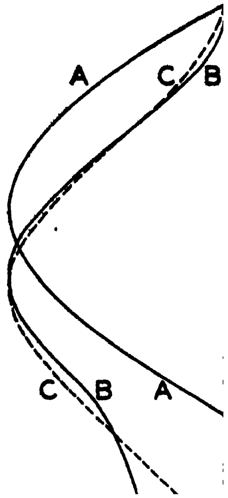


FIG. 4. *Current distribution in 0 597λ mast. A—Sinusoidal distribution. B—Experimentally measured curve of Gihring and Brown. C—Empirical distribution used in later calculations.*

$$I(x) = \frac{I_{\text{Loop}}}{2}\left[1 + \sin\frac{2\pi}{\lambda_0}\left(x - \frac{\lambda_0}{10}\right)\right]$$

where $\lambda_0 = 0.716\lambda$.

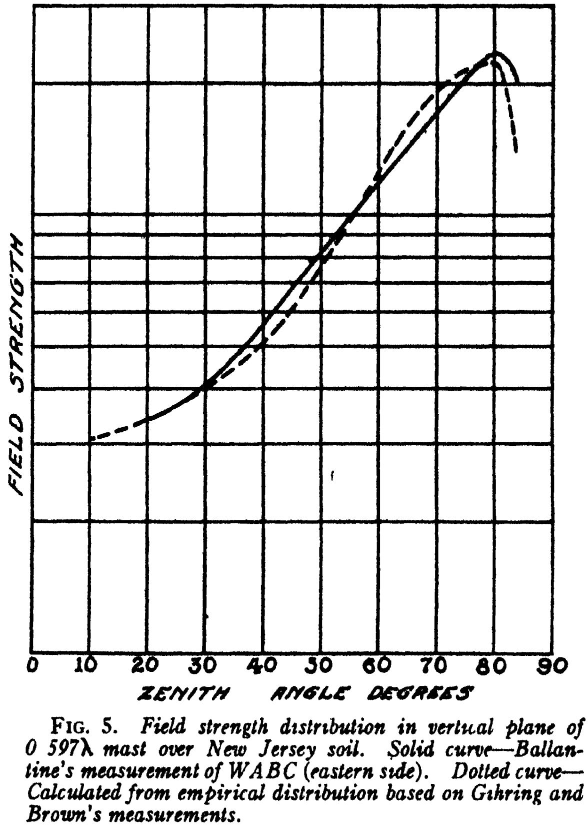


FIG. 5. *Field strength distribution in vertical plane of 0 597λ mast over New Jersey soil. Solid curve—Ballantine's measurement of WABC (eastern side). Dotted curve—Calculated from empirical distribution based on Gihring and Brown's measurements.*

Calculations using this $I(x)$, a frequency of 860 kilocycles, and New Jersey soil characteristics gives E_θ as indicated by the dotted curve of Fig. 5. The solid curve of Fig. 5 is a graphical representation of Ballantine's measurements on the eastern side of WABC. The agreement* is striking, especially when it is found that the assumption of a slightly lower conductivity for the soil will straighten out the dotted curve so that it will not depart so much from the solid curve at 45° and 68°. Fig. 6 shows the same calculated curve and Ballantine's measurements for the western side of WABC. Why there should be such a great difference between the fields on the west and east sides is not apparent. Differences in the soil characteristics (σ, ϵ) on either side cannot explain it.

In applying this parallel ray method (large r_0) to Ballantine's experiment (measurements made at a constant altitude of 4000 ft.), it can be shown that the error is negligible. Likewise considering the problem in the light of the developments of van der Pol and Niessen (5), it seems that the author's results should be applicable to Ballantine's results up to zenith angles of the order of 70°. In any case, the interest here lies only in the range of zenith angles up to 50°, as this range includes the lobe and minimum in field strength which a sinusoidal antenna current distribution demands, and of which experiment yields no sign.

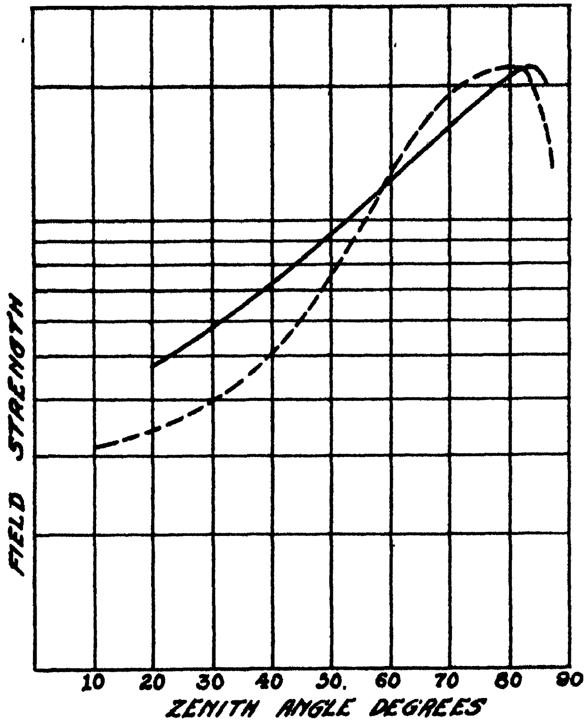


FIG. 6. *Field strength distribution in vertical plane of 0.597λ mast over New Jersey soil. Solid curve—Ballantine's measurement of WABC (western side). Dotted curve—Calculated for empirical distribution based on Gihring and Brown's measurements.*

Current Distribution in the Array Towers

As this current distribution of Gihring and Brown checks so well with Ballantine's measurements, and as it also checked with measurements of Gihring and Brown on another such radiator, it seems safe to assume that this distribution will be valid generally for this type of 0.597λ tower.

As regards the current distribution in the quarter-wave tower used as the reflector, calculations by the above method show that the difference in the shape of the field strength curves of a quarter-wave tower and of a quarter-wave wire is slight. Hence sinusoidal current distribution is assumed in the quarter-wave reflector.

Calculations for the Array

Assume that the 0.25λ reflector with current distribution $I'(x)$, height l', is placed a distance d from the 0.597λ radiator with current distribution $I(x)$, height $l : x'$ is the variable distance up the reflector from the ground; x is the variable distance up the radiator. Assume also that the quarter-wave tower is fed $\phi°$ in phase ahead of the other tower.

Then in the vertical plane containing the array

$$dE_\theta = \frac{2\pi}{cr_0\lambda} I'(x)\,dx' \sin\theta \left[\cos\frac{2\pi}{\lambda}(ct - r_0 + x'\cos\theta + d\sin\theta + \phi) + R\cos\frac{2\pi}{\lambda}(ct - r_0 - x'\cos\theta + d\sin\theta + \phi)\right]$$

$$+ \frac{2\pi}{cr_0\lambda} I(x)\,dx \sin\theta \left[\cos\frac{2\pi}{\lambda}(ct - r_0 + x\cos\theta) + R\cos\frac{2\pi}{\lambda}(ct - r_0 - x\cos\theta)\right] \cdot$$

Letting

$$a = \frac{2\pi x}{\lambda}\cos\theta \qquad b = \frac{2\pi}{\lambda}(d\sin\theta) + \phi$$

and rearranging, the following expressions are obtained

$$\frac{dE_\theta}{\sin\theta} \propto \cos\frac{2\pi}{\lambda}(ct - r_0)\left\{ \begin{array}{l} (R+1)\,[I(x)\cos a\,dx + \cos b\, I'(x)\cos a'\,dx'] \\ \quad + (R-1)\,[\sin b\, I'(x)\sin a'\,dx'] \end{array} \right\}$$

$$+ \sin\frac{2\pi}{\lambda}(ct - r_0)\left\{ \begin{array}{l} (R+1)\,[-\sin b\, I'(x)\cos a'\,dx'] \\ \quad + (R-1)\,[\cos b\, I'(x)\sin a'\,dx' + I(x)\sin a\,dx] \end{array} \right\}$$

$$\underset{r.m.s.}{E_\theta} \propto \sin\theta \sqrt{ \left\{ \begin{array}{l} (R+1)\left[\int_0^l I(x)\cos a\,dx + \cos b \int_0^{l'} I'(x)\cos a'\,dx'\right] \\ \quad + (R-1)\left[\sin b \int_0^l I'(x)\sin a'\,dx'\right] \end{array} \right\}^2 + \left\{ \begin{array}{l} (R+1)\left[-\sin b \int_0^{l'} I'(x)\cos a'\,dx'\right] \\ \quad + (R-1)\left[\cos b \int_0^l I'(x)\sin a'\,dx' + \int_0^l I(x)\sin a\,dx\right] \end{array} \right\}^2 }$$

where $l = 0.597\lambda$ and $l' = 0.25\lambda$

Constants for the Array

For purposes of calculation the following constants were assumed:— frequency, 700 kilocycles; ground conductivity, 10^{-13} e.m.u.; ground dielectric constant, 14 e.s.u.

The current distribution in the 0.597λ mast was taken to be the empirical distribution of Fig. 4 based on the experimental measurements of Gihring and Brown. That is,

$$I(x) = \frac{I_{\text{Loop}}}{2}\left[1 + \sin\frac{2\pi}{\lambda_0}\left(x - \frac{\lambda_0}{10}\right)\right]$$

where $\lambda_0 = 0.716\lambda$.

The sinusoidal distribution assumed in the 0.25λ tower is

$$I'(x) = I'_{\text{Loop}}\left[\sin\frac{2\pi}{\lambda}\left(\frac{\lambda}{4} - x'\right)\right].$$

In order to select the spacing d and phasing ϕ, it is necessary to decide on the zenith angle at which minimum radiation is desired. Assuming that 70° is the angle, then a likely choice of array constants is

$$d = \frac{\lambda}{4}\,\text{cosec } 70^\circ \qquad \phi = 90^\circ.$$

The remaining array constant, the ratio of the loop currents, is decided after introducing all the above values into the array equation. A good minimum is then seen to be possible for the quarter-wave loop current equal to 1.5 times the 0.597 wave loop current.

Comments on Results of Array Calculations

The relative values of E_θ for the above conditions have been calculated for every 10° zenith angle. The resulting curve is given in Fig. 7. This gives the field strength distribution in the vertical plane passing through the array.

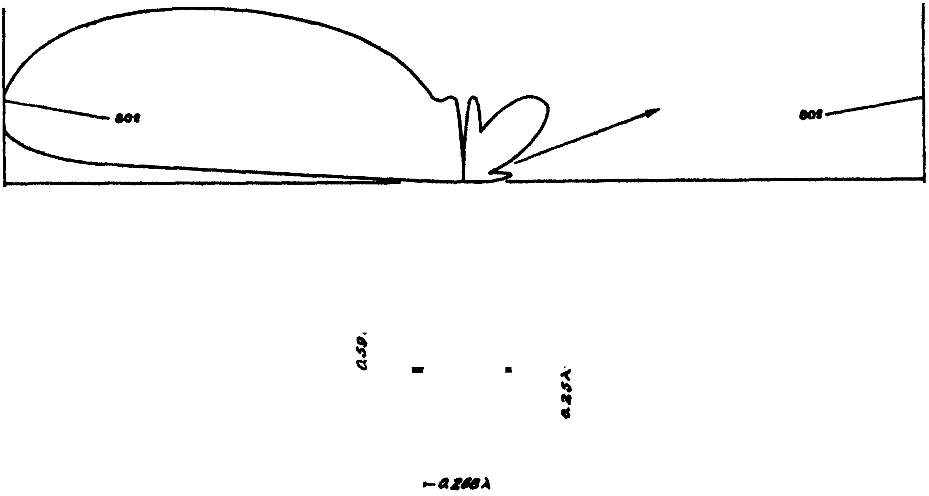


FIG. 7. *Field strength distribution in the vertical plane parallel to an array comprised of a 0.597λ double-tapered tower with a quarter-wave self-supporting tower as a fed reflector.*

CONDITIONS

Frequency: = 700 kc.
Soil constants: $\sigma = 10^{-13}$ e.m.u.
$\epsilon = 14$ e.s.u.
Current distribution in 0.597λ mast:

$$I(x) = \frac{I_{\text{Loop}}}{2}\left[1 + \sin\frac{2\pi}{\lambda_0}\left(x - \frac{\lambda_0}{10}\right)\right]$$

where $\lambda_0 = 0.716\lambda$.
Current distribution in 0.25λ mast:

$$I'(x) = I'_{\text{Loop}}\left[\sin\frac{2\pi}{\lambda}(l - x)\right].$$

ARRAY CONSTANTS

Spacing: $\frac{\lambda}{4}$ sec. 20°
Phasing: 0.25λ mast current 90° ahead of that of 0.597λ mast.
Current ratio: 0.25λ loop current = 1.5 of 0.597λ loop current.

Fig. 8 gives the distribution in the vertical plane perpendicular to the plane of the array. In this case d is zero.

Returning to Fig. 7, it is seen that almost complete extinction has been achieved at 70°, and in fact from 60° to 85° zenith angle the radiated power is very small. This broad minimum is advantageous as it would take care of variations in the height of the Heaviside layer, the average height being used

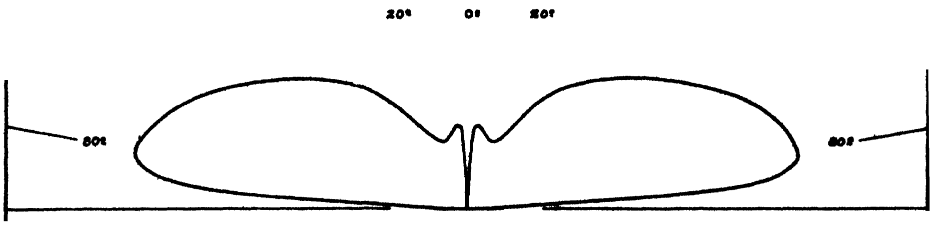
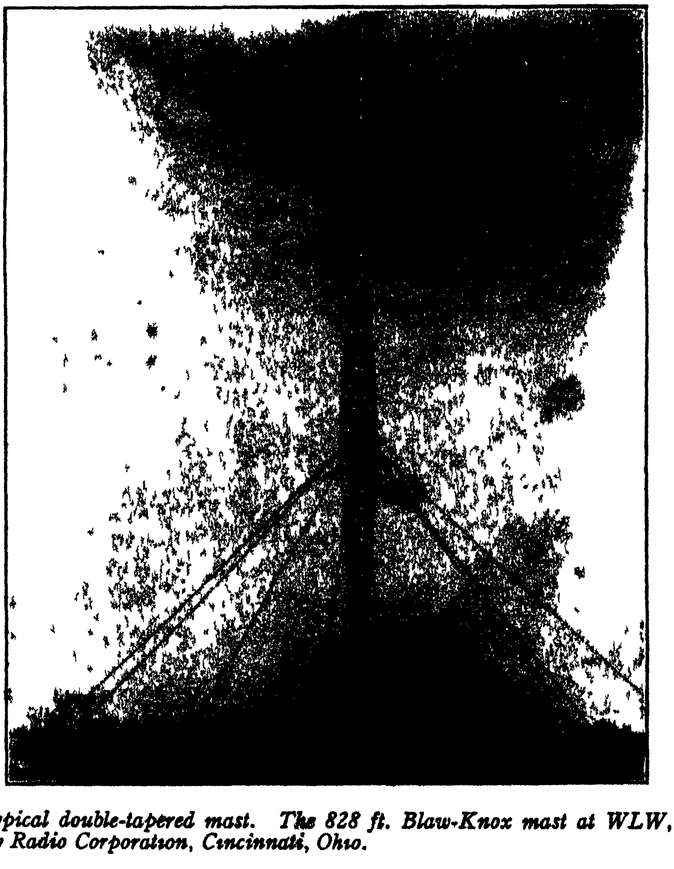


FIG. 8 *Field strength distribution in vertical plane perpendicular to the above array.*

to determine the zenith angle at which minimum radiation should occur. The large lobe at 45° would be expected to intersect the earth's surface about 200 miles away. Severe fading would occur about 100 miles from the high powered station. In the other directions it is seen that the polar pattern differs from that of the single mast in that there is relatively more high angle radiation.



A typical double-tapered mast. The 828 ft. Blaw-Knox mast at WLW, the Crosley Radio Corporation, Cincinnati, Ohio.

Conclusion

The calculations indicate that the array is efficacious in reducing the sky wave at zenith angles between 60° and 85°. The local coverage in the unfavored direction, however, is very unsatisfactory with the array constants chosen. Thus an increase in the ground wave and a decrease in the high angle lobe can be achieved by decreasing the ratio of the quarter-wave tower loop current to the 0.597 wave tower loop current. Other choices of spacing and phasing are also available.

It is concluded, therefore, that by a judicious choice of the three array constants a considerable reduction in the sky wave at remote distances can be achieved, whilst still maintaining fair local coverage in the unfavored direction.

Acknowledgment

The author wishes to acknowledge his indebtedness to Lieut.-Col. W. A. Steel, who suggested the problem, for his continued interest, and to Mr. J. A. Ouimet, for his assistance in some of the computations.

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AN X-RAY POWDER CAMERA FOR SPECIMENS AT VARIOUS KNOWN TEMPERATURES[1]

BY W. H. BARNES[2] AND W. F. HAMPTON[3]

Abstract

An X-ray camera designed specifically for pin-hole photographs of frozen gelatin gels at temperatures between 0° and −60° C. is described. The novel feature of the camera is the method of mounting the specimen on the surface of a copper block, the temperature of which depends on a controllable circulation of acetone at a controllable temperature. The adaptability of the camera to modifications required by specific conditions of specimen or temperature other than those for which it was primarily designed is pointed out. It is shown that the camera appears to be suitable for the study of a great variety of materials over a considerable temperature range both below and above 0° C., whenever a single crystal spectrograph, or an ionization spectrometer, is not required.

Introduction

During a recent X-ray examination of frozen gelatin gels, the results of which are described in detail elsewhere (1), it was necessary to obtain X-ray diffraction patterns of specimens at constant known temperatures below 0° C. Although the camera described in the present paper was designed, constructed and used for this purpose, it appears to be applicable to the study of a great variety of materials over a considerable temperature range both below and above 0° C. whenever a single crystal spectrograph, or an ionization spectrometer, is not required. The following description of the camera and the constant temperature system, however, will be confined to the arrangement at present in use for gelatin gels over the range 0° to −60° C. Extensions and modifications required by other materials and for other temperatures will be indicated at the end of the paper.

Description of the Camera

Base and Cooling Block

The base of the camera and the cooling block on which the specimen under examination is placed are shown in Fig. 1. The base, *A*, consists of a brass plate, $9\frac{5}{8}$ by $6\frac{5}{32}$ in., supported horizontally on four leveling screws, *B*, the feet of which rest on a platform above the X-ray tube. A suitable hole in this platform allows radiation from the tube to impinge vertically on the under side of the base, where a sheet of lead $\frac{1}{8}$ in. thick protects the camera above from unwanted radiation.

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[1] *Manuscript received August 20, 1935.*
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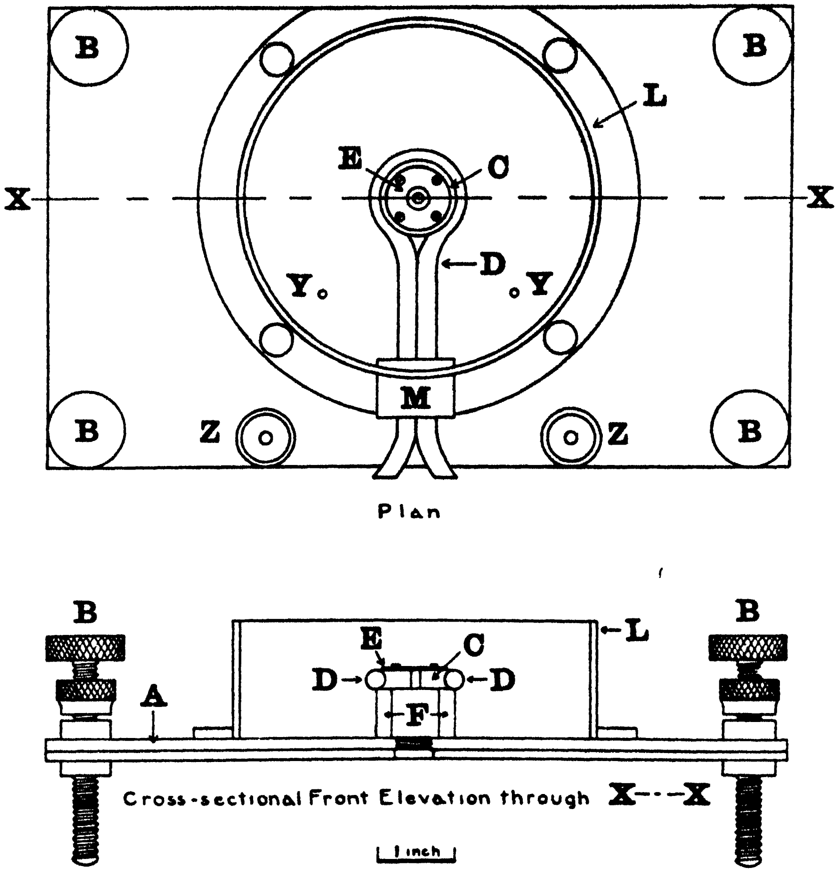

FIG. 1. *Base, cooling block and main plate-holder support.*

The cooling block, *C*, is a circular sheet of copper, 1 in. in diameter and ¼ in. thick, in a groove around the circumference of which is soldered a copper tube, *D*, of ¼ in. outside diameter. The specimen under examination is placed on the block, *C*, and over a 3 mm. hole that passes vertically through the centre of the block. A thin copper washer, *E*, 2 cm. outside and 7 mm. inside diameter, placed over the sample and fastened to the cooling block with four copper screws as shown in Fig. 1, serves to hold the specimen in position and ensures good thermal contact of the lower and upper surfaces of the specimen with the cooling block. It may be noted that the areas of the washer, *E*, and of the cooling block, *C*, in contact with the specimen, are greater than the cross-sectional areas of the holes through them. The temperature of the sample is controlled by that of the cooling block, which in turn depends on that of a suitable liquid circulating through the tube, *D*.

The cooling block is supported above the base, *A*, and is insulated thermally therefrom by a bakelite tube, *F*, ⅝ in. high and $\frac{7}{32}$ in. wall thickness, to which it is fixed by two flat-headed countersunk brass screws (not shown in Fig. 1). Four similar screws hold the bakelite tube to the base, *A*.

Pin-hole System

The pin hole system is shown in Fig. 2. The brass tube, *G*, $1\frac{7}{8}$ in. long and $\frac{5}{16}$ in. internal diameter, passes through a hole in the lead sheet and screws into the base, *A*, of the camera. It is held in place by the lock-nut *H*. The axis of the tube is normal to the upper surface of the base, *A*, and to the upper surface of the cooling block, *C*, and passes through the centre of the hole in the latter and of that in the copper washer, *E*.

Pin holes of various diameters for definition of the X-ray beam are made by filling the ends of brass tubes (such as *I* in Fig. 2), of length about $2\frac{3}{16}$ in., with lead, and boring holes of the diameters desired through the lead and along the axis of the tubes. The pin-hole tubes are machined to a sliding fit inside the tube, *G*. When a given set of pin holes is to be employed the appropriate tube, *I*, is inserted in the tube, *G*, so that a brass ring, *J*, $\frac{5}{8}$ in. from the lower end of the tube, *I*, is in contact with the lower end of the tube, *G*, where it is fixed in position with the special lock-nut *K*. In this position the upper pin hole is close to the under side of the cooling block, *C*, and the axis of the pin holes is normal to the upper surface of this block, and passes through the centre of the hole therein.

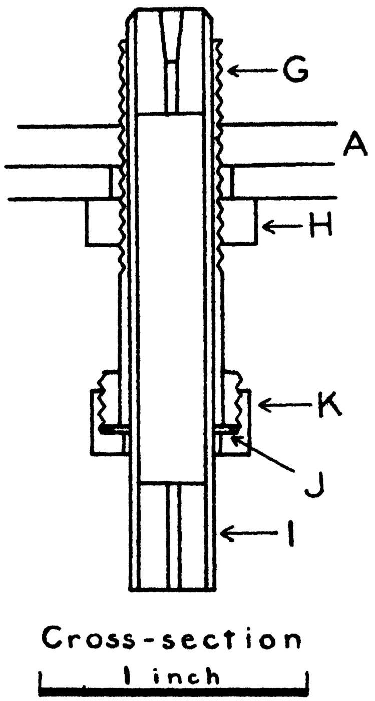

FIG. 2. *Pin-hole system.*

The upper half of the pin-hole nearer the specimen is tapered as shown in Fig. 2, in order to prevent radiation diffracted by the edges of the pin hole from entering the camera.

Plate-holder Support

For the shortest crystal-to-plate distance (about 2.2 cm.) the plate holder is supported on a brass tube *L* (see Fig. 1), which is fixed to the base, *A*, of the camera by means of a flange and four thumb-screws. This tube is $1\frac{1}{2}$ in. high, $4\frac{3}{4}$ in. outside diameter, and has a wall thickness of $\frac{3}{32}$ in., and its upper edge is normal to the axis of the pin-hole system with which also its axis coincides.

The ends of the copper cooling tube, *D*, are insulated thermally from the tube, *L*, where they emerge from the camera, by the hard-rubber plug *M*.

Different crystal-to-plate distances may be obtained by the use of a set of brass tubes, *N*, of appropriate heights, which make sliding fits inside the tube, *L*. By means of the slot *O* (see Fig. 3) they may be inserted in the tube, *L*, until their lower edges rest on the base of the camera. In this position their upper edges are normal to the axis of the pin-hole system,

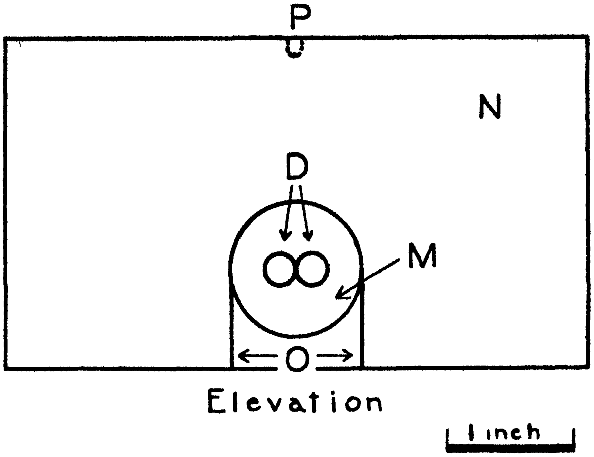

FIG. 3. *Subsidiary plate-holder support.*

and that area of the slot *O* which is not closed by the plug is covered by the tube *L*.

A small slot, *P*, in the upper edge of the tube *N*, is required for one of the parts of the plate holder.

Plate Holder

The plate holder is shown in Fig. 4. The brass ring *Q* fits closely over either the main plate-holder support *L* (Fig. 1), or the tube *N* (Fig. 3). The alumi-

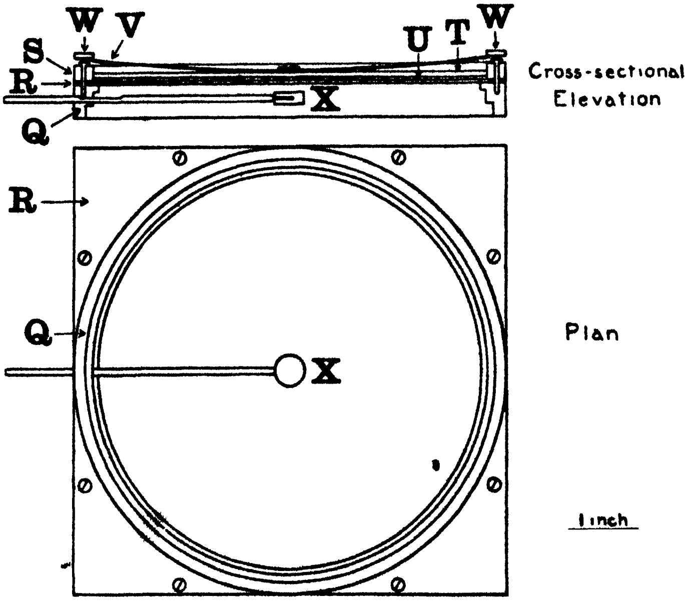

FIG. 4. *Plate holder.*

nium plate *R* and the aluminium frame *S* are fixed to this ring with screws. A hole in the former, of the same diameter as the smallest inside diameter of the ring *Q*, is covered with a sheet of black light-proof paper which is fastened between the plate *R* and the frame *S*.

The back of the plate holder is an aluminium plate *T*, $\frac{1}{16}$ in. thick, which fits closely inside the frame *S*, and is lined with a piece of felt, *U*. It is held in place by two pieces of spring brass, *V*, which are free to rotate about their centres. When the plate holder is loaded, the ends of these strips are pressed under the heads of large flat-headed screws, *W*, protruding from the frame, *S*.

The comparatively deep frame *S* ($\frac{3}{8}$ in.) permits the use of films or plates, with, or without, a backing intensification screen, while the spring clips ensure firm contact in all cases between the film or plate and the front of the plate holder.

The undiffracted portion of the incident X-ray beam is prevented, if desired, from impinging on the photographic emulsion by lead buttons, *X*, $\frac{1}{8}$ in. thick and of diameters depending on the size of the pin holes and the crystal-to-plate distance employed. These buttons may be screwed on the end of a brass rod, $\frac{3}{32}$ in. in diameter, which passes through a hole in the brass ring *Q*. By means of a screw through the ring *Q*, the end of which is in contact with a flattened section of this rod, the lead button, *X*, may be pulled back out of the path of the incident X-ray beam, or pushed forward into a fixed position in which it absorbs the beam, without disturbing the plate holder. This rod fits the small slot *P* in the upper edge of the tube *N* (Fig. 3), and when the plate holder is in position this slot is covered completely.

Description of the Cooling System

As mentioned above, the temperature of the specimen on the cooling block, *C*, is controlled by circulating a suitable liquid at any desired temperature through the cooling tube *D*. For the present experiments at temperatures between 0° and $-60°$ C., acetone has been employed as the circulating liquid and a mixture of solid carbon dioxide and acetone as the cooling medium.

The closed circulation system at present in use is represented diagrammatically, and not to scale, in Fig. 5. A volume of about 200 cc. of acetone is circulated continuously by means of the pump *e* through the coils *i* and *j*, which are packed in a mixture of solid carbon dioxide and acetone, thence through a heating coil *k*, and finally through the cooling tube *D* around the cooling block, *C*, in the camera, and back to the pump *e*. The acetone flows through the system at a very steady rate, leaves the coil *j* at a constant low temperature and is warmed to the temperature desired by means of a constant current in the heating element *k*. Very steady temperatures of the cooling block, *C*, are obtained by this method, and the temperature can readily be adjusted by altering the rate of flow of the acetone and varying the current through the heating element.

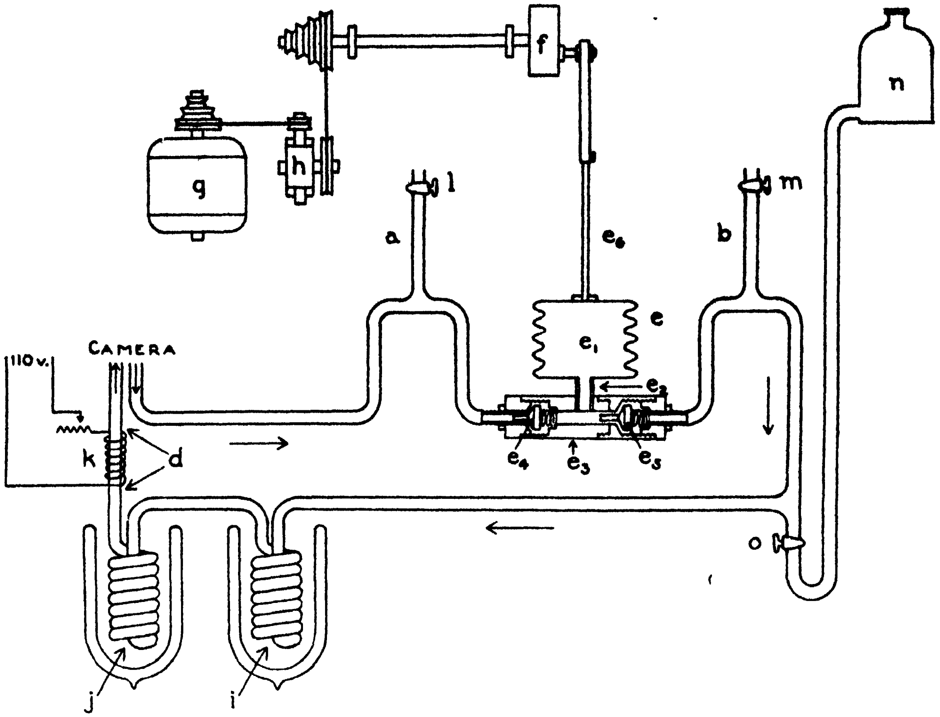

FIG. 5. *Closed circulation system for cooling the specimens.*

The acetone flows through ¼ in. copper tubing, with the exception of sections *a*, *b*, *c* and *d*, the first three of which are made of soft glass and the last of Pyrex. All sections of tubing except these are heat insulated with asbestos, and the connections between sections are made with heavy walled $\frac{3}{16}$ in. rubber tubing. This has proved to be quite satisfactory and is more amenable to alterations in the system than metal connections proved to be.

The pump, *e*, consists of a 2½ in. length of 2 in. copper bellows tubing, e_1, the ends of which are closed with brass sheet. A short length of ¼ in. brass tubing, e_2, connects the inside of the bellows to a hole through a length of 1 in. square rod, e_3, the ends of which are fitted with the inlet and outlet valves, e_4 and e_5, respectively. These valves are held in position against their seats by light, coiled springs. The pump is fixed to a rigid wooden base by means of a brass flange at the back of the square rod e_3.

The rod e_6, attached to the centre of the brass sheet at the upper end of the bellows, e_1, is held by a set-screw in a brass tube which constitutes the pivoted arm of an adjustable eccentric, *f*. The eccentric is driven by a 110 volt d-c. shunt wound motor, *g* (max. speed rating, 1800 r.p.m.), acting through a fixed reduction gear, *h*, and two sets of pulleys, as shown schematically in Fig. 5. The displacement of the pump may be varied by means of the adjustable eccentric, while a wide variation in speed of operation is provided by a variable resistance in the field circuit of the motor, and by the sets of pulleys on the motor and eccentric drive shafts, respectively.

Each of the cooling coils *i* and *j* is in the form of a spiral wound from 25 ft. of ¼ in. copper tubing. Two coils set up in separate Dewar flasks are in use so that, since the maximum rate of consumption of solid carbon dioxide occurs around coil *i*, the supply of solid carbon dioxide can be replenished in the first Dewar flask without disturbing the temperature equilibrium of the system.

The heating element, *k*, consists of a coil of 10 ft. of nichrome wire (23 B. & S.) wound over the asbestos-covered length of Pyrex tubing *d*. Suitable known currents may be passed through the coil, *k*, by means of a slide-wire rheostat in the main (110 volt d.c.) electrical supply circuit.

The distances between the cooling coil *j* and the heating element, *k*, and between the latter and the tube *D* in the camera, are as short as possible.

The cooling system is filled by opening the taps *l*, *m*, and *o*, in the tubes *a*, *b*, and *c*. Acetone flows into the system from the storage aspirator bottle, *n*, and the displaced air escapes through the tubes *a* and *b*. These tubes and the pump, *e*, are above the level of all other points in the closed cooling circuit. When acetone appears in the tubes *a* and *b*, the taps *l*, *m*, and *o* are closed and the pump *e* is brought into operation. The resulting circulation of acetone drives any air remaining in the system into the tubes *a* and *b*. From time to time the taps *l*, *m*, and *o* are opened and this accumulated air is replaced by acetone. After a few minutes operation no more air appears in the tubes *a* and *b* and the system is ready for use.

In practice a small volume of air is allowed to remain in the tubes *a* and *b* to serve as an air cushion and thus ensure a steadier flow of acetone when the pump is in operation. A small head of liquid also is supplied by having the acetone levels in *a* and *b* above that of the pump, thus facilitating the operation of the valves e_4 and e_5. When the temperature of the acetone is reduced, the resulting decrease in volume is counteracted by the addition of more acetone from the storage bottle, *n*, through the tap *o*.

Temperature Measurement and Control

The temperature of the sample is determined by means of a copper-constantan thermocouple and a Cambridge portable type potentiometer. The fixed temperature junction of the thermocouple is immersed in an ice-water mixture, while the other junction is placed between the specimen under investigation and the cooling block, *C*, in the camera (Fig. 1). The washer *E* ensures good contact between the specimen, the thermocouple junction, and the cooling block. Insulated leads from this junction pass out of the camera through the small holes, *Y*, in the base, *A*, and thence between the base, *A*, and the lead sheet to the edge of the base where they are brought up to the binding posts, *Z*. These binding posts are equipped with specially designed hard-rubber washers for electrical and thermal insulation of the ends of the leads. Lengths of the same wires connect the fixed temperature junction and the potentiometer with these binding posts. In this way the camera may be transported if necessary without moving the entire thermocouple circuit.

As previously mentioned the temperature of the specimen is controlled by varying the displacement of the pump, *e*, its speed of operation, and the current in the heating element, *k*. The e.m.f's. generated by the thermocouple are observed continuously during an exposure and the temperature is adjusted accordingly. It has been found, however, that once the desired temperature has been attained the cooling system seldom requires any further attention, and will maintain the temperature constant (at least to 0.1 or 0.2° C.) for several hours without further adjustment.

It may be mentioned that in regulating the temperature it is desirable to keep the number of strokes of the pump per unit time as large as possible, in order to maintain as steady a flow of acetone as possible through the system.

Discussion

Since the camera described in this paper was designed primarily for specimens at temperatures below 0° C., it was necessary that it should be vapor tight. This was effected by covering the line of contact between the plate-holder support, *L*, and the base, *A*, and those between the plug, *M*, the plate-holder support, *L*, and the tube *D* with plasticine. All lines of contact inside the camera where diffusion of water vapor from the outside to the inside might occur, were smeared with petroleum jelly as were also the outsides of the tubes *N* and *I*, respectively. The pin hole nearer the X-ray tube was covered with a thin sheet of moisture-proof cellophane, and another thin sheet of the same material was stretched across the front of the plate holder and held in position between the ring *Q* and the plate *R*. With these precautions a negligible deposition of frost takes place on the cooling block *C* and the tube *D* even after several hours at a low temperature. This small amount can be prevented from forming, if desired, by removing the moisture from the air in the camera by means of a small dish of phosphorus pentoxide placed therein before reducing the temperature of the cooling block.

As pointed out previously, the present camera is readily applicable to the study of materials other than gels at temperatures other than those below 0° C. For temperatures between about −15° C. and room temperature the cooling coils *i* and *j* may be packed in mixtures of calcium or sodium chloride and crushed ice. For higher temperatures the acetone in the circulating system may be replaced by water or other suitable liquid, and the coils *i* and *j* immersed in automatically controlled oil thermostats at a temperature slightly below the one required. If desired the heating element *k* and the tube *d* may be removed, and the temperature of the specimen regulated by adjusting that of the thermostats around the coils *i* and *j*.

The camera is suitable for the study of almost any kind of material by the monochromatic pin-hole method. It may also be employed for Laue photographs if the crystal has a well developed face normal to the axis along which it is desired that the X-ray beam should pass.

Gels, metal foils, papers, etc., which do not require a special support, are placed on the cooling block so that they cover the 3 mm. hole and are there held in position by the washer *E*. Powdered specimens may be placed on a strip of thin metal foil, cellophane or mica, the last, if diffraction rings from the first two interfere with the pattern from the specimen under investigation. Alternatively the powder may be mixed with an amorphous binder and pressed into a thin sheet. Liquids may be placed in a shallow copper frame with a mica bottom.

If a larger range of 2θ angles than that possible with the use of a flat plate holder is desired, the plate-holder support, *L*, may be replaced by a semi-cylindrical film-holder of 10 cm. radius which can be fastened to the base, *A*, with thumb-screws in such a position that the sample is at the centre of curvature of the film. A slit system instead of pin holes may be incorporated in the tube *I*.

The camera, therefore, appears to lend itself readily to such modifications as may be required by specific conditions other than those for which it was primarily designed.

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VIBRATIONS OF POWER LINES IN A STEADY WIND

I. THE ALTERNATING FORCES EXERTED BY THE WIND[1]

By R. Ruedy[2]

Abstract

The theory of the structure of eddies formed in a steady wind at the surface of a wire placed at a right-angle to the direction of the wind shows that the alternating force exerted upon the obstacle is proportional to the diameter d of the wire and to the square of the wind velocity U. The force is of the same order of magnitude as the drag in the direction of flow, but changes sign with the formation of each new eddy near the obstacle.

When the expression for the force is introduced into the equation of motion of the vibrating string, and damping by the air is taken into account, the computed amplitudes, A, proportional to the force and inversely proportional to the damping coefficient and the frequency, agree with the small amplitudes observed in the field in moderate winds and known by experience to damage the cables near the support. The result may be expressed as $A \propto d^{\frac{3}{2}} U^{\frac{1}{2}}$.

Introduction

The fact that musical sounds are produced when the wind flows past a stretched wire or similar obstacle of suitable length was known in Biblical times, but the relation between the speed U of the wind, the thickness d of the wire and the frequency f of the sound was established only in 1878 for wires about 1 mm. thick and velocities of a few metres per second (8). The frequency is higher the faster the wind and the thinner the string, so that approximately

$$f \doteqdot 0\ 2\frac{U}{d},$$

U and d being expressed in the same units. Somewhat smaller values are obtained in light winds and also for wires less than 0.03 cm. in diameter. Providing that the speed of the wind exceeds a few metres per second, the sound reaches its greatest intensity when the frequency f approaches one of the resonance frequencies of the wire. By fastening the wire upon a frame and whirling it around, more than 25 overtones can be produced in succession, not all of them, however, with the same strength (8). The tentative explanation suggested at the time, namely, that the sound is due to internal friction which forces air masses to detach themselves from the wire, was confirmed long afterwards through studies on the double row of eddies forming behind the wire in running water and in air and their relation to the steady resistance presented by the body if it is not streamlined (2–5, 9, 10).

The alternating component of the effect, on the other hand, has within the last ten years become of direct practical importance in connection with transmission lines. With conductors being made thicker and thicker, in some cases nearly five centimetres in diameter, the small vibrations caused

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Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

[2] *Research Investigator, National Research Laboratories.*

by light but steady winds, often during more than one-half of the year, have been found by engineers almost without fail to damage the cable in the long run and cause breaks by fatigue near the supports. On account of the considerable amount of experimental work carried out for a number of years, by power companies and cable manufacturers, in the laboratory as well as in the field, on these small vibrations of less than one inch amplitude, it seems worth while to develop the theory of the typical vibrations produced by air eddies in so far as they are of practical interest. To this end it is necessary to ascertain the alternating forces exerted in a vertical direction upon a wire placed in a horizontal wind, at right angles to the direction in which it blows, and to study the influence of air-damping, hitherto considered as a negligible factor, upon the vibration. It will then be possible to find what amplitudes are to be expected under the influence of a steady wind.

The Forces Exerted upon a Cylinder by the Malloch-Karman Trail of Eddies

When a steady wind strikes the cylindrical surface of a stiff wire, the lines of flow are distorted; they curve upward and downward so as to avoid the obstacle. The centrifugal forces that are set up on both sides of the cylinder create a pressure against the wire. The changes in the streamlines on the upstream side of the cylinder might be expected to be duplicated but in the opposite sense on the downstream side, so as to neutralize their effects, were it not for forces of inertia and the energy lost by internal friction. The slower portions close to the surface of the wire are dragged along by the outer layers, so that the streamlines join less readily behind the obstacle than they spread on meeting it. As a consequence, air is pushed from the downstream side into the voids which tend to form, and eddies are set up near the body at the surface of contact between the masses which move in opposite directions. In the steady state these eddies follow one another alternately first on one and then on the other side of the diameter that lies parallel to the direction of the stream, or on the upper and the lower side when the wire is placed in a horizontal position—and move downstream, more slowly, though, than the air. At some distance from the body, the ratio u/U of the common velocity of the eddies, u, to the velocity U of the undisturbed air stream becomes nearly constant and equal to about 0.14 for a circular cylinder, while the distance l between the eddies lying on the same line is about 3.2 times the distance h which separates the two series of eddies and which, as is to be expected, is only slightly larger than the diameter of the cylinder (3). If one eddy rotates in one direction the eddy following it on the other side of the track rotates in the opposite direction. Considerable energy is required to establish and maintain these whirls and, while, when the fluid merely creeps, the resistance offered by an obstacle is due entirely to friction and is proportional to the velocity, at higher speeds the resistance is produced by internal friction and eddy motion until finally the flow becomes turbulent. At any point in the system of vortices on the downstream side of the obstacle, the velocities in the U- or x-, and y-directions, when a spot half-way between two contrary vortices and far from the obstacle itself is taken as the origin (Fig. 1), are for an observer at rest:

$$v_x = \frac{\Gamma}{2l}\left(\frac{\sinh\frac{2\pi}{l}\left(y+\frac{h}{2}\right)}{\cosh\frac{2\pi}{l}\left(y+\frac{h}{2}\right)-\cos\frac{2\pi}{l}\left(x+\frac{l}{4}\right)} - \frac{\sinh\frac{2\pi}{l}\left(y-\frac{h}{2}\right)}{\cosh\frac{2\pi}{l}\left(y-\frac{h}{2}\right)-\cos\frac{2\pi}{l}\left(x-\frac{l}{4}\right)}\right)$$

$$v_y = \frac{\Gamma}{2l}\left(\frac{\sin\frac{2\pi}{l}\left(x+\frac{l}{4}\right)}{\cosh\frac{2\pi}{l}\left(y+\frac{h}{2}\right)-\cos\frac{2\pi}{l}\left(x+\frac{l}{4}\right)} - \frac{\sin\frac{2\pi}{l}\left(x-\frac{l}{4}\right)}{\cosh\frac{2\pi}{l}\left(y-\frac{h}{2}\right)-\cos\frac{2\pi}{l}\left(x-\frac{l}{4}\right)}\right),$$

or

$$v_x = \frac{\Gamma}{2l}\left(\frac{\sinh\frac{2\pi}{l}\left(y+\frac{h}{2}\right)}{\cosh\frac{2\pi}{l}\left(y+\frac{h}{2}\right)+\sin\frac{2\pi}{l}x} - \frac{\sinh\frac{2\pi}{l}\left(y-\frac{h}{2}\right)}{\cosh\frac{2\pi}{l}\left(y-\frac{h}{2}\right)-\sin\frac{2\pi}{l}x}\right)$$

$$-v_y = \frac{\Gamma}{2l}\left(\frac{\cos\frac{2\pi}{l}x}{\sin\frac{2\pi}{l}x+\cosh\frac{2\pi}{l}\left(y+\frac{h}{2}\right)} - \frac{\cos\frac{2\pi}{l}x}{\sin\frac{2\pi}{l}x-\cosh\frac{2\pi}{l}\left(y-\frac{h}{2}\right)}\right)$$

where in the steady state $\Gamma = ul\sqrt{8} = 2.82\,ul$, apart from the sign.

The two components of the velocity are by no means alike. The component along the x-axis remains positive in the space between the paths followed by the two rows of eddies, that is, between $y = +h/2$ and $y = -h/2$, and becomes negative in part of the outer portions of the eddies, but is never negative throughout the width of a section having a given value of y. On

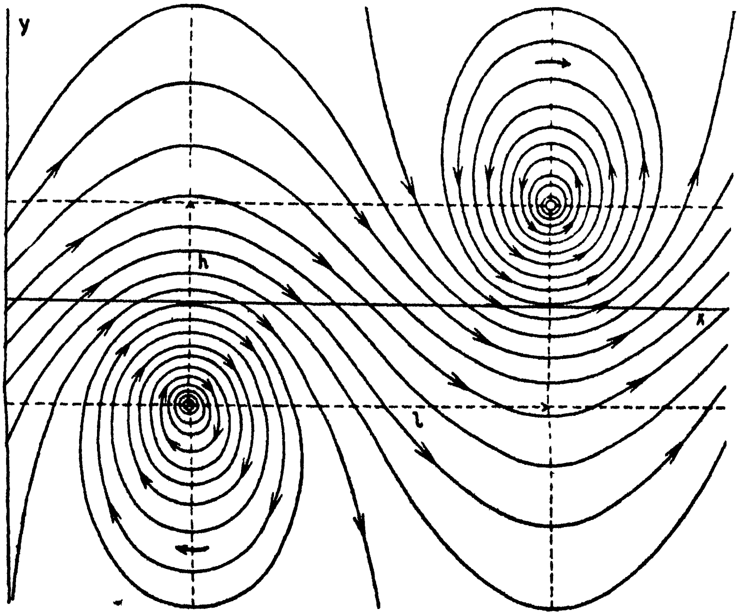

FIG. 1. *Eddies produced on the downstream side of a cylindrical obstacle of diameter $d \doteq h$, placed to the left of the origin so as to be normal to the flow along the x-axis.*

the other hand, the component v_y along the y-axis is negative between $x = 0$ and $x = l/4$, whatever the value of y, positive in the strip between $x = l/4$ and $x = 3l/4$, and changes sign once more in the last quarter of the section. Moreover, two points at the same level y, but a distance $l/2$ apart, have the same speed parallel to y, but in opposite directions (Fig. 1). Broadly speaking, there is thus an upward rush of air one-half of the time and a similar downward motion during the rest of the time. Both v_x and v_y return to the same values after each distance $x = l$, or taking into account the time required for the eddy system to traverse this length, after $l/(U - u)$ seconds, for an observer moving with the eddy system. At the end of any such period, conditions are the same as before except that a new pair of eddies has joined the procession. The excess of momentum, J, produced in unit time per unit length of the cylinder, along the x- and y-axes in the disturbed region, over that in the corresponding section ahead of the obstacle, must be derived from forces of friction acting upon the body by way of the boundary layers. Now for any one strip of density ρ parallel to y

$$\Delta J_x = \rho \int_{x=0}^{x=l/2} dx \int_{-\infty}^{+\infty} v_x dy$$

and

$$\Delta J_y = \rho \int_{x=0}^{x=l/2} dx \int_{-\infty}^{+\infty} v_y dy \quad .$$

The summation is extended to infinity although the extreme limits of y may instead be taken equal to $+2h$ and $-2h$, if desired, since beyond this distance the eddy motion actually vanishes. With

$$\tan^{-1}\left(\tan\left(\frac{\pi}{2} - \frac{a}{2}\right)\right) = \frac{\pi}{2} - \frac{a}{2} \qquad \text{or} \qquad \frac{3\pi}{2} - \frac{a}{2},$$

$$\int \frac{\sin a}{\cosh z - \cos a} dz = 2 \tan^{-1}\left(\operatorname{cotan}\frac{a}{2} \tanh\frac{z}{2}\right) = 2 \tan^{-1}\left(\tan\left(\frac{\pi}{2} - \frac{a}{2}\right) \tanh\frac{z}{2}\right)$$

and

$$\int_{-\infty}^{+\infty} v_y dy = \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{2\pi}{l} x + \frac{\pi}{2}\right)}{\cosh\frac{2\pi}{l}\left(y + \frac{h}{2}\right) - \cos\left(\frac{2\pi}{l} x + \frac{\pi}{2}\right)}$$

$$- \int_{-\infty}^{+\infty} \frac{\sin\left(\frac{2\pi}{l} x - \frac{\pi}{2}\right)}{\cosh\frac{2\pi}{l}\left(y - \frac{h}{2}\right) - \cos\left(\frac{2\pi}{l} x - \frac{\pi}{2}\right)} = \pm \frac{\Gamma}{2} \, .$$

If the positive sign applies to the space between two eddies of opposite sense, the negative sign applies to the space between the next two eddies. Apart from the sign, the momentum is constant for one layer, so that for the strip $l/2$ cm. long the total increase of momentum per second per unit height of the obstacle, is:

$$\frac{\Delta J_y}{\Delta t} = \pm \frac{\rho}{4}(U - u)\Gamma \, .$$

This value must be considered as produced by a steady force acting upon the cylinder in the y-direction; expressed in dynes per unit length it can be written as

$$P = \pm \frac{\rho}{4} U\left(1 - \frac{u}{U}\right)\Gamma = 1.2\rho U^2 h\ ,$$

and is therefore proportional to the square of the wind velocity U (measured in cm. per sec.). It also increases with the thickness of the cylinder inasmuch as the width of the track of eddies, h, increases of course with the diameter of the obstacle. This conclusion seems to be in agreement with experiment (4).

The experiment shows that d/l is equal to about 0.23 so that

$$\frac{1}{\tau} = \frac{U-u}{l} = \frac{Ud}{ld}(1 - u/U) \doteq 0.2\,\frac{U}{d} = f\ .$$

Since, moreover, for each interval $0 < t < \tau/2$,

$$1 = \frac{4}{\pi}\left(\sin\frac{2\pi}{\tau}t + \frac{1}{3}\sin 3\,\frac{2\pi}{\tau}t + \frac{1}{5}\sin 5\,\frac{2\pi}{\tau}t + \ldots.\right),$$

the force P may be written and considered as the sum of sine waves, the first and strongest of which has the same period as the force:

$$P = 0.215\,\rho\Gamma U\left(\sin pt + \frac{1}{3}\sin 3\,pt + \frac{1}{5}\sin 5\,pt + \ldots.\right).$$

The force acting upon the cylinder in the x-direction has been determined by the same method. Since

$$\int v_x dy = \int \frac{\sinh\frac{2\pi}{l}\left(y \pm \frac{h}{2}\right)}{\cosh\frac{2\pi}{l}\left(y \pm \frac{h}{2}\right) \pm \sin\frac{2\pi}{l}x}\,dy = \frac{l}{2\pi}\,ln\left(\cosh\frac{2\pi}{l}\left(y \pm \frac{h}{2}\right) \pm \sin\frac{2\pi}{l}x\right),$$

and for any one point $y = mh$, when m is a large number,

$$\int_{-mh}^{+mh} v_x dy = 2\int_0^{mh} v_x dy = \frac{\Gamma}{2l}\,\frac{l}{\pi}\,ln\,\frac{\cosh\frac{2\pi}{l}h(2m+1)}{\cosh\frac{2\pi}{l}h(2m-1)} \doteq \frac{h\Gamma}{l},$$

it follows that, for any one layer parallel to the y-axis, the momentum is constant as to sign and magnitude. For the space occupied by one pair of eddies, therefore,

$$\frac{\Delta J_x}{\Delta t} = \rho(U-u)\,\frac{h}{l}\,\Gamma = 1.132\,\frac{\Delta J_y}{\Delta t}\ .$$

This value is equal to the steady force exerted by the stream upon the cylinder as a result of the formation of eddies. It forms an appreciable fraction of the total resistance, D, per unit length offered by the cylinder in the direction of the x-axis, namely (3)

$$D = \rho\Gamma\frac{h}{l}(U-u) - \rho\Gamma\frac{h}{l}u + \rho\frac{\Gamma^2}{2\pi l} = \rho l U^2\left(0.794\,\frac{u}{U} - 0.\pi\left(\frac{u}{U}\right)^2\right),$$

since

$$\frac{\frac{\Gamma h}{l}\,U\left(1 - \frac{u}{U}\right)}{\frac{\Gamma^2}{2\pi l} - \Gamma\frac{h}{l}u} = 0.59$$

As given, the expressions depend only on constants belonging to the trail of eddies; but in practical applications the resistance or the drag is often referred to the diameter of the cylinder and the velocity in the form

$$D = c\rho d \frac{U^2}{2},$$

where, therefore,

$$c = 2\left(0.794 \frac{u}{U} - 0.\pi \left(\frac{u}{U}\right)^2\right) \frac{l}{d}.$$

Since d/l is equal to 0.23, the drag coefficient c becomes equal to about 0.92. In pounds per foot of length of the cylinder, this expression corresponds roughly to $D = dV^2/5000$, where d is in inches and V in miles per hour.

The alternating force P acting in the y-direction can be transformed in the same way and becomes

$$P = \pm\, 2.83 \frac{\rho U}{4}\left(1 - \frac{u}{U}\right) ul = 0.085 \rho U^2 \frac{l}{d} d \doteq 0.73\, \rho d \frac{U^2}{2}$$

per unit length of the cylinder. The amplitude of the fundamental component of the force may, therefore, be taken as equal to 0.93 $\rho d U^2/2$. A series of measurements on the damping of pendulums immersed in various fluids has given, in place of the coefficient 0.93 in the formula for the maximum strength of the cross force, values ranging between 0.61 and 1.05, the average being 0.94 for cylinders ranging in thickness from 0.64 to 1.67 cm. (10).

When d and U are expressed in centimetres and the density is put equal to 1.25×10^{-3} at 10° C. and 760 mm. of mercury, the force is obtained in dynes per unit length. When d and U are measured in metres and ρ is put equal to about $\frac{1}{8}$ kg. per cu. metre, the force is obtained in kilograms (-force).

Range of Validity of the Theory

The forces in the y-direction have not yet been measured directly, but the drag, D, obtained in the x-direction has been studied over a wide range. In the expression

$$D = c\rho \frac{U^2}{2} d$$

per unit length, c is a factor which, experiments show, depends on Reynolds', number, R:

$$R = \frac{vd}{\nu} = vd\frac{\rho}{\eta} = \frac{l^3 \rho v^3}{l^3 \eta v} = \frac{\text{Kinetic energy}}{\text{Work against friction}},$$

where η is the coefficient of internal friction. When the diameter, d, is expressed in centimetres and the speed, v, in centimetres per second, $1/\nu \doteq 7$ at 10° C. The exact value depends on the temperature and on the pressure. Starting with a low Reynolds number, R, in which case the effects of internal friction predominate, the value of c for a long cylinder is large, but decreasing (9, p. 97). Between $R = 1/10$ and $R = 1$, it drops from 60 to about 10. At $R = 100$ its value is 1.43 and at $R = 1000$ it is only 0.93. Beyond $R = 10^{-4}$, but $R < 10^5$, it is fairly constant and equal to 1.2, so that the resistance is nearly proportional to the square of the velocity between $R = 10^3$ and $R = 10^5$. This is the region in which the theory of the eddy structure accounts for the measured drag.

When R exceeds 2×10^5, the value of c drops rapidly and reaches approximately 0.3 (at $R = 4 \times 10^5$) only to increase again, though slowly, above this point. The flow in this range is turbulent.

With diameters, d, from 0.5 cm. or less to several centimetres, and wind speeds between a fraction of a kilometre to 50 and more kilometres per hour, the corresponding Reynolds numbers vary between about 1000 ($d = 1$ cm., $v = 140$ cm. per sec., a "wind" that is not felt as such) and 100,000, that is, they fall into the range where the square law formula holds. Experience shows, however, that when the wind velocity exceeds about 20 km. per hr. (550 cm. per sec.), and possibly even at lower velocities, the speed is found to vary from point to point and vibration ceases, so that the range within which the resistance formula applies without restriction to long cylinders exposed to the wind lies between the Reynolds number 1000 (for which $c = 1$) and 50,000 (for which $c = 1.2$). Work in wind tunnels is usually carried out at higher values, R being about 5×10^5.

Amplitude of the Vibrations

The steady detachment of eddies which are formed by the wind causes the conductor to vibrate in a vertical plane. There is of course no doubt that when displaced by the eddies the wire in turn modifies the eddies. But for the small displacements currently observed in practice, a few centimetres at the most on loops several metres long, and for the usual low frequencies, not more than 100 cycles per second, the motion of the wire is slow compared with that of the wind, so that the forces computed for the stiff cylinder are also exerted upon the flexible line. The line begins to resonate when the eddy frequency, which remains

$$f \div 0.2 \frac{U}{d},$$

approaches one of the resonance frequencies of the stretched conductor. The speed, U, in the present case exceeds 100 cm. per sec. (two miles per hour), the velocity at which the wind makes itself just felt. As the velocity of the wind increases from 100 to 1000 cm. per sec., the eddy frequency for a wire 2 cm. thick varies from 10 to 100 per second, that is, it belongs to the vibrations forming the lowest audible range. On the other hand, the fundamental frequency in the plane of the span varies for high voltage lines between a fraction of a cycle and about two cycles per second, so that the procession of eddies excites only very high harmonics in the span.

In order to establish the effects of a steady wind upon the span, the conductor is conveniently considered as a string to which the required external tension is applied, displacements in the plane of the span being measured from the position of equilibrium and parallel to the vertical. A comparison of observed and computed amplitudes, however, is justified only if allowance is made for damping by friction.

If m is the mass per unit length of a stretched string or of a catenary, and a force $mY(\sigma, t)d\sigma$ acts at the time t on an element of length $d\sigma$ of the string in addition to a damping force proportional to the velocity, the partial differential equation of motion is (11)

$$m\frac{\partial^2 u}{\partial t^2} + r\frac{\partial u}{\partial t} + T\frac{\partial^2 u}{\partial \sigma^2} = mY(\sigma,t),$$

or, writing $c^2 = T/m$,

$$\frac{\partial^2 u}{\partial t^2} + 2k\frac{\partial u}{\partial t} - c^2\frac{\partial^2 u}{\partial \sigma^2} = Y(\sigma,t)$$

Assuming $Y(\sigma,t)$, the force exerted upon unit length and unit mass, to be a periodic force $Y \sin pt$, where p corresponds to the eddy frequency, a particular solution of the equation giving the displacement u in the vertical, may be given as

$$u = \frac{Y}{D_t^2 + 2kD_t - c^2D_\sigma^2}\sin pt \sin \kappa\pi\frac{\sigma}{s},$$

where κ is an integer, s the length of the curve described by the conductor, while D_t is the symbol for $\partial/\partial t$, and D_σ, the symbol for $\partial/\partial\sigma$(11). Restricting the solution to sine waves

$$u = Y\sin\kappa\pi\frac{\sigma}{s}\,\frac{\left(\kappa^2\pi^2\frac{c^2}{s^2} - p^2\right)\sin pt - 2kp\cos pt}{\left(\kappa^2\pi^2\frac{c^2}{s^2} - p^2\right)^2 - 4k^2p^2}.$$

In the general case the motion u consists of a sum of such terms with different values of κ. The highest amplitude of a wave of angular frequency $\kappa\pi\frac{c}{s} = 2\pi f$ is

$$A_{\kappa m} = \frac{Y}{2k\kappa\pi\frac{c}{s}} = \frac{Y}{4\pi kf} \doteq 0.08\frac{Y}{kf},$$

and is reached when

$$p^2 = \kappa^2\pi^2\frac{c^2}{s^2} - 2k^2 \doteq \kappa^2\pi^2\frac{c^2}{s^2},$$

provided that this expression is positive, a condition always satisfied when k is decidedly less than the critical damping coefficient, $\kappa\pi c/2s$, or the resonance frequency. The term approximately corresponding to resonance between the external frequency and one of the natural frequencies of the wire in the absence of damping is the only value that is of practical importance As soon as Y and k are known the theory may be compared directly with the scattered observations on conductors that have been made under favorable conditions.

a. Damping for Small Amplitudes

When the Reynolds number, R, corresponding to the average velocity of the vibrating string is smaller than unity, the damping coefficient k, that is, the natural logarithm of the ratio between successive amplitudes multiplied by the frequency, is given by a formula derived by Stokes (12, p. 105)

$$k = \frac{4\sqrt{\pi\rho f\eta}}{\rho_0 d}$$

In this formula, η is the viscosity of the air (1.77×10^{-5} at 10° C.), ρ its density (1.25×10^{-3} at 10° C.), and ρ_0 the density of the material from which the string is made. For quiet air at about 10° C.

$$k = \frac{0.0033\sqrt{f}}{\rho_0 d}.$$

Since k includes only the effects due to internal friction in air, it represents the smallest possible value of the damping coefficient. For a given frequency, damping becomes pronounced when the wire is very thin and of a light material. But even tor aluminium lines, the damping coefficient is but slightly larger than $f^{\frac{1}{2}}/1000d$. Overtones are more strongly damped than the fundamental.

Table I shows observed and computed values for a steel string 58.9 cm. long and 0.081 cm. thick ($\rho_0 = 7.8$) tuned in turn to two different frequencies (6). The amplitude of the vibration, obtained in this case by means of an electromagnet, was of the order of 0.01 cm. The measured damping coefficients are higher than the computed coefficients, but calculation of the Reynolds numbers for the highest velocity $v = 2\pi fA$ (in place of the average velocity $4fA$) of points on the loop shows that the condition that R be smaller than unity is not fulfilled over an appreciable length of the string during an appreciable fraction of the period, so that higher values are to be expected for k.

TABLE I

MEASURED AND COMPUTED VALUES OF THE DAMPING COEFFICIENT, k, FOR A STEEL STRING 0.081 CM. THICK, 58.9 CM. LONG, $\rho_0 = 7.8$. (AMPLITUDES ABOUT 0 01 CM.)

Frequency, cycles/sec.	Number of loops	k		v_m	R_m	$v_{av.}$	$R_{av.}$
		Obs.	Calcd.				
252	2	0.18	0.08	15 8	8.9	6 3	3 5
505	4	0.25	0 12	31 7	17.8	12 6	7 1
635	5	0.51	0 13	39 9	22.3	16	9 0
904	7	0.81	0.16	56.8	31.8	22 6	12 7
230	1	0 23	0.08	14 4	8.1	6	3.6
462	2	0 33	0 12	29.0	16.3	12	7.2
694	3	0 28	0 14	43.6	24 4	17 4	10 9
928	4	0.37	0.16	58.3	32.6	23	14.5

$v_{av.} = 2.5 fA$. $v_m = 6.28 fA$.

Table II gives the damping coefficient, k, and the amplitude, A, in cm., as computed for one of the wires used in the early experiments on sounds produced by the wind (8). The Reynolds number has been calculated for the average velocity $v \doteqdot 2.5 fA$ in the loop. The last two columns contain the average frictional resistance, $2kmv$, entering into the equation of motion, and the air resistance, D, for the same velocity, v, but, in place of the alternating, a steady motion. For cylinders, the resistance to be overcome when displacing them in quiet air is (9, p. 97)

$$D = \frac{4\pi\eta}{2.002 - lnR} U,$$

as long as $R \leq 1$.

TABLE II

COMPUTED VALUES OF DAMPING COEFFICIENT k AND AMPLITUDE A FOR A WIND-DRIVEN WIRE OF BRASS (0 05 CM. THICK, 73.6 CM. LONG, $\rho_0 = 8.4$)

U cm./sec.	f cycles/sec.	k per sec.	Y dynes	$A_{av.}$ cm.	$v_{av.}$ cm./sec.	$R_{av.}$	$2kmv$	D
244	706	0 22	25 0	0.013	22.9	8	0 67	0.04
287	885	0 25	34 6		29.0	10	1.0	0.08
331	1062	0 27	46.0		34 5	12	1.2	0.08
397	1330	0.31	66 2		43.2	15	1.8	
445	1513	0.32	83.2		49.1	17	2.1	

b. Damping for Large Amplitudes

Since the alternating force acting in the wind upon a wire is proportional to the diameter, d, and the square of the speed, U, of the wind, and with the frequency at resonance proportional to the ratio U/d, the amplitude, A, is given by

$$A = \frac{Y}{4\pi fk} = \alpha\, d^{\frac{3}{2}}\, U^{\frac{1}{2}}\, \rho^{\frac{1}{2}}\, \eta^{-\frac{1}{2}}$$

where α is a constant for a given wire. The amplitude increases but slowly with the wind velocity, particularly in high winds, but more rapidly with the thickness of the wire, a diameter 10 times larger producing an amplitude 31.6 times larger at, of course, a frequency 10 times lower. When, however, the displacements exceed a few millimetres and the frequencies are as usual above 10 cycles per second, the resistance of the air increases, the damping forces tending to become proportional to the square of the velocity of motion in place of being proportional to the velocity. Pending a more detailed investigation, an approximate value of the damping coefficient may be deduced by observing that at $R = 1$, where $D = 2\pi\eta U$, the formula for k may be written

$$k = \frac{2\sqrt{2\rho f D/U}}{\rho_0 d}\,.$$

Assuming that in this form the formula is also valid for larger values of R, for instance, in the range of the eddy trail, where

$$D \doteqdot \tfrac{1}{2}\rho d v^2,$$

a new value is obtained for the damping coefficient which is $(\rho dv/4\pi\eta)^{\frac{1}{2}}$ times larger than k, or about $5\sqrt{dv}$ times larger than k. Damping coefficients of this order give, even for thick conductors, amplitudes that do not exceed a few centimetres, or displacements of the magnitude observed in the field.

Comparison with Observations in the Field

Since the frequencies excited in the conductor by light winds amount to at least 20 cycles per second, when $U = 100$ cm. per sec. and $d = 1$ cm., and correspond to high overtones, a change of only 5 cm. per sec. in the speed of the wind produces in the course of time the next higher overtone. Wind-strengths are very seldom steady to within a few per cent, so that standing loops and nodes that form on the line tend to shift about in an irregular way, each vibration taking, of course, a certain time to become fully established. Moreover, when the eddy frequency falls midway between two overtones, the winds excite both harmonics to about the same extent. In other cases, the speed of the wind changes gradually along the span (1, p. 257). Hence the records from vibrating lines show, more often than not, the existence of several vibrations and beats such as are produced by two neighboring frequencies (7).

Among the large number of records taken on power lines, there are very few giving a steady amplitude at a single frequency (7). For instance, a steel-reinforced aluminium conductor 1.43 cm. in diameter has been found to vibrate with an amplitude of nearly 0.25 cm. in a wind of three miles per hour (169 cm. per sec.) blowing at almost a right-angle to the line (75°). The Reynolds number corresponding to the highest velocity of points on the loop (36 cm. per sec., the frequency being 23 cycles per sec.), is about 350, and hence beyond the range where the formula for k is valid ($k = 0.004$). With a force $Y = 3.7\rho d U^2/\rho_0 \pi d^2$ acting upon unit mass, the correct amplitude results for a damping factor k equal to 0.08, which, as shown by experiment, is a reasonable value for cables of this type.

It seems, therefore, that the trail of eddies accounts not only for the frequency, but also for the amplitudes of the vibrations set up in wires by a steady wind.

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* *A mistake of —100 was made in the numbering of the pages at the end of Ann. Physik, 77. The pages given here should have been 727-757.*

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A NOTE ON THE SPECTROSCOPIC DETERMINATION OF THE VITAMIN A CONTENT OF PILCHARD OIL[1]

BY G. M. SHRUM[2] AND THOMAS G. HOW[3]

Abstract

An attempt has been made to measure spectroscopically the Vitamin A content of pilchard oil. Using the same conversion factor as for cod liver oil, measurements of the extinction coefficient at 3280Å gave Vitamin A values much larger than those obtained by biological tests. It has been shown that this discrepancy cannot be wholly ascribed to either the coloring matter or the saponifiable material in the oil. A satisfactory check on the results can be obtained only when it is possible to remove completely the Vitamin A from the oil, without otherwise modifying it.

Introduction

It has been fairly well established that Vitamin A concentrates and oils of high Vitamin A potency give a constant ratio among the results of the biological, chemical and physical methods for the determination of the Vitamin A content (2, 3, 6). Since spectroscopic measurements are relatively easy to make and at the same time tend to give the highest degree of accuracy (7), it seemed worth while to try to extend this method to measurements of the Vitamin A content of lower potency oils. This report deals chiefly with such an attempt, the oil under investigation being British Columbia pilchard oil. Some preliminary results are given to indicate the possibilities of the method. A more extended analysis can be made only when a greater number of biologically tested samples are available.

For high potency oils the Vitamin A content in 1934 International Vitamin A units can be obtained from the extinction coefficient at 3280Å by using a suitable conversion factor. The extinction coefficient, k, is defined by the equation $I = I_0 10^{-kx}$, where I_0 is the light incident on the absorbing solution and I that which is transmitted through x cm. of the solution. The value of this coefficient at 3280°A was determined by a visual method, using a fluorescent screen, and also photographically. Where it was necessary to obtain k for different wave-lengths, absorption spectra were obtained with the use of a step-sector and a quartz spectrograph.

Experimental

The most convenient method for determining k was found to be the visual method. It included the use of a copper arc, a filter which transmitted a narrow band at 3280Å, a fluorescent screen and some mechanism for controlling the intensity of the incident light. Such a method has been developed by Adam Hilger, Ltd., and the apparatus named a "Vitameter A." An instrument somewhat similar in design was constructed and used in this work. While, in the "Vitameter A," a cylindrical lens and rectangular aperture are used for adjusting the intensity, in this instrument the variation in intensity is controlled by an adjustable sector. The instrument is shown in diagram in Fig. 1. A is a copper arc run at 3 amp. on a d-c. circuit of 110 volts; B_1 and B_2 are two small circular apertures; C is a light filter consisting of a silvered quartz window which transmits a narrow band of radiation at 3280Å (9); D is a cell containing the solution under examination; E is an adjustable sector; F is a fluorescent screen of canary glass. A compensating glass plate, G, is placed in the beam which does not pass through the solution. By varying the adjustable sector the intensity of the light passing through B_2 can be varied, and the two images at F can thus be brought to the same brightness. From the angular setting of the sector, $\log \frac{I_0}{I}$ can be found, and hence k. The sector was run at a speed of 30 rev. per sec., sufficiently fast so that there was no flicker. Talbot's law, which states that, "the apparent intensity of an intermittent light is proportional to the time of each individual flash, provided there is no flicker," would then hold.

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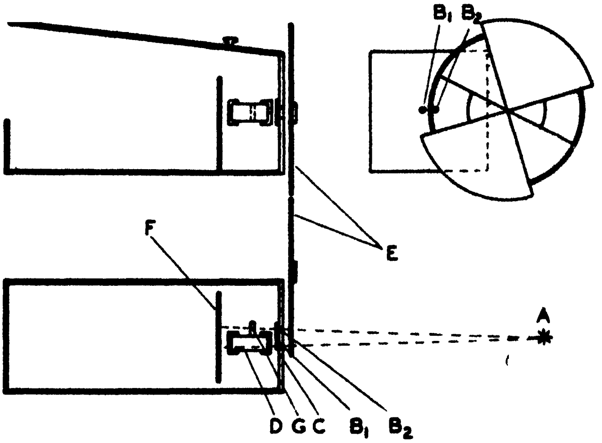

FIG. 1. *Arrangement of the apparatus for visual spectrophotometry at 3280Å. A, copper arc; B_1, B_2, circular apertures; C, a silvered quartz filter; D, cell for the solution; E, an adjustable sector; F, a fluorescent screen of uranium glass; G, a compensating glass plate.*

The order of accuracy of such a determination can best be shown by graph A, Fig. 2, plotted to illustrate Beer's law, which postulates a linear relation between extinction coefficient and concentration. The concentration is given in terms of the number of grams of oil per 100 gm. of the cyclohexane which was used as solvent. Values of $\log \frac{I_0}{I}$ plotted on the graph were average values of five readings which seldom deviated more than 5% from the mean. This visual method was checked by finding k photographically,

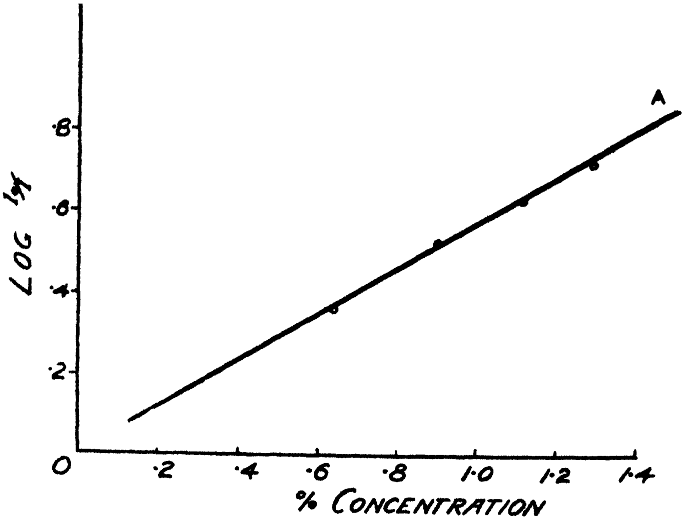

FIG. 2. *Graph showing the linear relation between log I_0/I and concentration.*

using for the purpose the well known Hilger sector photometer (4). Table I shows how the two methods agreed for a sample of pilchard oil. When it was necessary to determine the absorption spectrum over a wider range, a photographic method with a step-sector (5) was used. Fig. 3 shows diagrammatically the arrangement of the apparatus. By means of a sphero-cylindrical lens, light from an iron arc was condensed upon the slit of a quartz spectrograph (Hilger E. 1) in such a way that

TABLE I

VISUAL DETERMINATIONS OF LOG I_0/I COMPARED WITH THOSE OBTAINED WITH SECTOR PHOTOMETER

Concentration, %	Visual method log I_0/I	Sector photometer log I_0/I
0.75	0.34	0.32
1.00	.51	.49
.43	.21	.21
.43	.21	.23

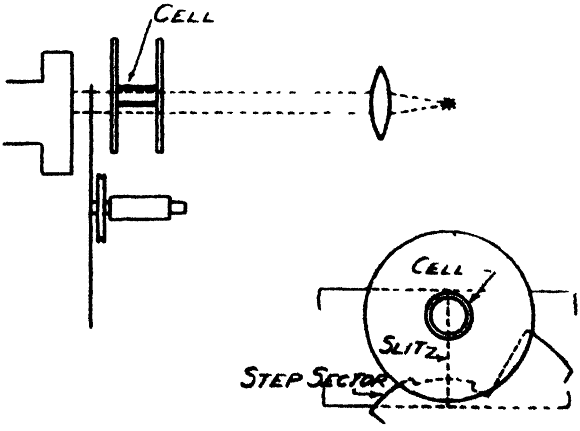

FIG. 3. *The arrangement of the absorption cell and the step-sector.*

the light remained parallel in the vertical plane. The absorption cell was placed close to the slit so that the resulting spectrum was divided into two sections, the light passing through the upper part of the slit being the radiation that had traversed the absorbing solution in the cell, and that incident on the lower part being the comparison beam. The calibration of the comparison beam was effected by means of the step-sector placed between the slit and the cell. The sector was arranged so that both beams were intermittent. The construction of the absorption cell did not eliminate errors due to reflection and absorption at the cell windows. However, these errors would not affect, materially, the shape of the absorption curve, within the wave-length range used in this work. A Moll microphotometer was used for measuring the densities of the plates.

As a solvent, spectroscopically pure cyclohexane was used throughout the experiment. Solutions were prepared and allowed to stand for 12 hr., otherwise different portions of the solution gave different values for *k*. The quartz windows were cemented with a commercial cement called "liquid solder," which has two advantageous properties. It is not soluble in cyclohexane, and it is easily removed when the cell is dismantled in order to clean it.

Results

Several samples of pilchard oil were studied. Two of these, as listed in Table II, were also tested biologically.* In order to check the method, a biologically tested cod liver oil and a standard solution of Vitamin A† were tested and the results included in Table II.

TABLE II

COMPARISON OF THE BIOLOGICAL AND PHYSICAL DETERMINATIONS OF VITAMIN A CONTENT

Sample	Vitamin A content	
	Biological	Physical
Standard solution	12,500	11,700
Cod liver oil	650	620
Pilchard oil No. 1	120	380
Pilchard oil No. 2	175	580

The second column in the table was obtained by multiplying the extinction coefficient for a 1% solution by a conversion factor of 1600. Somewhat lower values for the conversion factor have been used by some workers but this value gave a very good agreement, between our results and the biological tests, for the standard solution and the cod liver oil. In the case of the pilchard oil there is a very large discrepancy between the results obtained and the biological values. The high values given by the spectroscopic method must be caused by other absorbing substances in the oil. That such extraneous absorption is common in the oils of low Vitamin A potency has been observed by other workers (8). In many cases it has been shown to be due to the free fatty acids which can be eliminated by saponification. A sample of pilchard oil No. 1 was therefore saponified (1) and its absorption spectrum before and after saponification was obtained by the method previously described. These absorption curves are shown in Fig. 4. The extinction

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*On albino rats by B. E. Bailey of the Fisheries Experimental Station, Biological Board of Canada, Prince Rupert Station.

†Obtained from British Drug Houses, Ltd., through the courtesy of Charles Anders.

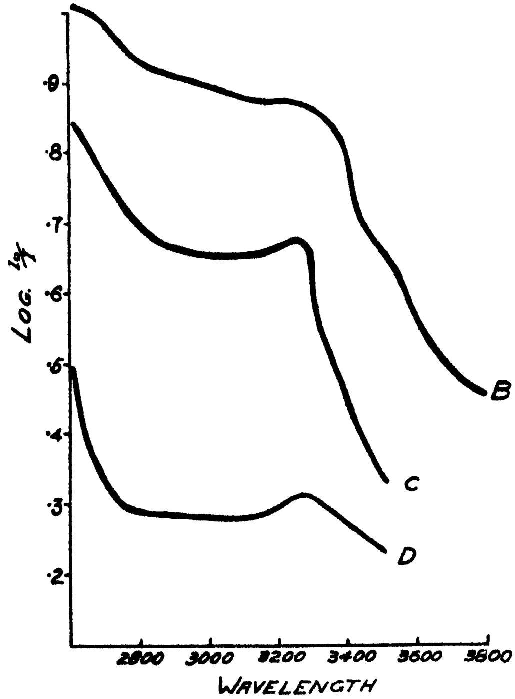

FIG. 4. *Absorption spectra of pilchard oil. Curve B, the normal oil; Curve C, the unsaponifiable fraction of the oil; Curve D, the unsaponifiable fraction of a sample in which the Vitamin A had been previously destroyed by oxidation at 90° C.*

coefficient at 3280Å, as determined from Curve *C*, was somewhat less than that given by Curve *B*, thus showing some absorption by fatty acids in the oil. However, the corrected value of the Vitamin A content, 300, was still too large to compare favorably with the biological assay of 120 units.

There was a further possibility that the pigment in the oil might have an absorption band near 3300Å. This was investigated by finding the extinction coefficient of the oil after decolorizing with diatomaceous earth. It was found that the decrease in *k* at 3280Å, after decolorizing the oil, was small. Since the action of diatomaceous earth is oxidizing as well as absorptive, it might be expected to remove some of the Vitamin A. The small decrease in absorption observed would indicate that the absorption at 3280Å of the pigment in the oil is negligible.

It was concluded that some other unsaponifiable material was the cause of the remaining discrepancy, and that if the Vitamin A could be eliminated from the oil, its unsaponifiable fraction would show an absorption at 3280Å which would be due to this unknown material. This absorption might then be subtracted from the value obtained in the preceding determination, and the difference should give a value for the true Vitamin A content. To eliminate the Vitamin A the oil was oxidized for five hours by bubbling air through it at 90° C. The unsaponifiable fraction was then studied spectroscopically. Curve *D* (Fig. 4) was thus obtained. The difference in the extinction coefficient at 3280Å between Curves *C* and *D* is equivalent to 160 units of Vitamin A, which corresponds more favorably with the biological value of 120 units. It may be observed that the absorption decreased not only at 3280Å but also lower down in the ultra-violet. This can be explained if it is assumed that some of the material which had an absorption band in the lower region was destroyed along with the Vitamin A. As its absorption band might extend to 3280Å the difference in the extinction coefficient at this wave-length between Curves *C* and *D* may not be due entirely to Vitamin A. The value of 160 units, therefore, obtained from this procedure is subject to a correction which can be ascertained only by treating the oil in such a way that the Vitamin A alone would be destroyed. Any method by which the Vitamin A could be removed from the oil without otherwise modifying it would provide a more accurate means of checking the results obtained by any spectroscopic method of analysis.

Acknowledgments

The authors take pleasure in acknowledging the co-operation and assistance given by Dr. Neal M. Carter and Mr. Basil E. Bailey of the Fisheries Experimental Station (Biological Board of Canada), Prince Rupert, B.C.

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VIBRATIONS OF POWER LINES IN A STEADY WIND

II. SUPPRESSION OF VIBRATIONS BY TUNED DAMPERS[1]

By R. Ruedy[2]

Abstract

Vibration of power lines is prevented by attaching in each span, at a distance b from the end, one or two dampers which consist in principle of a heavy mass M fastened to the end of a spring (Holst damper), or to both ends of a thin cantilever suspended at its centre, or to a cable (Stockbridge damper). The mathematical study of the forces in a span provided with a damper and subjected to a tension T furnishes the constants necessary for the proper designing of dampers. For an incoming angular frequency p, the ratio, undamped to damped amplitude, is in practice equal to $1 - p^2bMD/T$, where D is the ratio of the force exerted by a spring upon a solid support to the force applied to its mass. Dampers suspended at the end of the first quarter of the loop length and tuned to the frequency at which the conductor vibrates, suppress, from a practical standpoint, the motion of the entire span when their damping factor amounts to a few units and their weight is equal to the weight of a loop length of conductor. By choosing different frequencies for the dampers used on a given span, and by taking advantage of the coupling existing between them, a fairly wide band of frequencies may be suppressed.

Vibration and Fatigue Failures

In careful design the conductor in the spans of a power line is so strung that during the times of severest loads, which are to be expected at minimum temperature and with the worst ice coatings and the highest winds, the tension in the cable will not exceed a value of about 75 to 100% of the elastic limit of the metal in question. But the proportional limit and the breaking point refer to more or less immediate effects produced by the load. Indeed, when different loads are left suspended on rods or wires of the same size, a smaller load may cause a wire to break, providing that it be allowed to act for a longer time.

Like conditions prevail with respect to alternating forces. The endurance limit is defined as that stress per unit area that may be applied to a given material for an indefinitely large number of cycles without producing rupture, supposing, of course, that such a limit exists. The endurance limit is found by counting the number of cycles of pulling, bending or twisting that a sample stands without becoming damaged under different reversing forces, and by plotting the critical stress S, or its logarithm, as a function of the logarithm of N, the number of cycles. Plotting against the number of cycles is unreliable (6). For all wrought ferrous metals and for a certain number of light metals, such as rolled aluminium and extruded magnesium, the S *versus* log N graph for flexure shows a sharp bend as the load is reduced, and changes to the horizontal direction at less than 10 million cycles. For rolled aluminium the critical stress is given as 11,000 lb. per sq. in. in reversed flexure; the average tensile strength is about 30,000 lb. per sq. in. There is a second class of materials for which the curve representing the limiting stress as a function

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Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

[2] *Research Investigator, National Research Laboratories, Ottawa.*

of log N keeps falling even beyond the sharp bend of the curve. This behavior is shown by cold drawn copper, and to a slighter degree by annealed copper, but an endurance limit of about 10,000 lb. per sq. in. may somewhat arbitrarily be chosen (6). The tensile strength of hard drawn copper is 58,000 to 68,000 lb. per sq. in. For hot rolled unannealed Monel metal and duralumin the endurance limit is inversely proportional to the logarithm of the number of cycles throughout the entire range tested, up to at least 1000 million cycles. When a "wind" of 50 cm. per sec. blows against a power line of 1 cm. diameter, the eddy frequency $f = 0.2U/d$ is 10 cycles per sec. As a frequency of only one cycle per second corresponds to 86,400 cycles per day, an average of 100 days of continued feeble wind in the first year brings the number of vibrations which a newly strung conductor makes, well into the range of cycles for which the endurance limit, and not merely the tensile strength, has to be taken into account in designing the line. Failures appear in the form of fractures more or less perpendicular to the axis of the wire, with no sign of yielding as in ordinary overstressed pieces. Their number increases rapidly with time; if s failures are observed in the first year, as many as 2^8s failures occur after two years (1). The highest stresses are likely to be found near the clamps by which the wires are fastened, unless the core of the cable is made to act as a support for the conducting shell. Slight scratches, or hidden cracks and faults, aggravate the effects of fatigue.

In view of the uncertainty of the endurance limit, particularly in materials not always handled with the utmost care and exposed to corrosion and scratching, the safest method of prolonging the life of conductors seems to be to suppress vibrations as completely as possible, either by removing the causes or by rendering displacement more difficult.

Direct Methods of Suppressing Vibrations

The formation of eddies is prevented in struts used on aeroplanes by giving them drop-shaped or streamlined contours, but if this change were made in the case of transmission lines the greater curvature then obtained in certain portions of the cross-section would increase corona losses. A slight flattening should, however, overcome some of the difficulties and increase the damping. The only other remedy to prevent the formation of eddies is to shield the line from the wind: in hilly or wooded country vibrations give little trouble. In some exposed regions it will also be possible to have the power lines run along, and not across, the direction of the most frequent winds.

When it is not possible to prevent the formation of eddies, forces may be applied which directly oppose the impulses given by the eddies to the wire. The only force that lends itself readily to this end along the entire span is the horizontal component of the magnetic field of the earth, about 1/5 gauss. But even with currents of 100 to 200 amp. flowing in wires 2 to 3 cm. thick, the forces exerted by the magnetic field are but a few dynes per centimetre, or several times less than the forces that a low wind would produce, so that, quite apart from the difference in the frequency, this method does not offer an effective remedy.

It is not, however, necessary, in order to keep mechanical vibrations within bounds, to apply opposing forces along the entire length of the span. A periodic force $Q \cos pt$ acting at the single point $\sigma = b$ (or at the symmetrical point $\sigma = s - b$ near the other end of a string of length s) produces the same effect as a force $mP \cos pt d\sigma$ acting in opposite phase upon each element of mass $m d\sigma$ of the string, provided that the initial conditions, such as, for instance, the shape of the conductor, etc., be the same, and that, in addition (7, p. 187),

$$Q_b = \frac{msP}{\sin(\kappa\pi b/s)},$$

where κ is the number of loops. This equation, which is useful when an effort is made to reproduce by machine or by hand the vibrations caused by the wind, shows that the force required is small when it is applied in the centre of the loop where $b = l/2\kappa$. At a node, where $b = s/\kappa$ or a multiple of s/κ, even the most intense force is without effect. In any case the amplitudes become large only when the frequency of the applied force coincides with one of the resonance frequencies $\kappa(T/m)^{\frac{1}{2}}/s$ of the span, which is under a tension T.

The Tuned Spring Damper

While a system of relays controlled by the vibrating cable, the current and the wind could be used in serious cases to generate and apply the required opposing forces, it is simpler to let the point of application itself create the opposing force by attaching to it a spring carrying a weight, which is forced to move through a viscous fluid held in a vessel fastened to the string. The displacement of the suspension point stretches and compresses the spring in turn and creates an alternating force K that opposes the displacement in the rhythm of the vibration. Devices of this kind are variously called dynamic dampers, or absorbers, or resonance dampers with viscous damping. They act by a combination of the inertia of their mass, the elastic force and the resistance due to friction, and even when no wind is blowing and the conductor hangs quietly, the shape of the equilibrium curve is altered. In order to study the action of the spring damper it is therefore necessary to find for the vibration of the string, a solution that can be adapted to the changed initial shape created by the presence of the spring damper (Fig. 1).

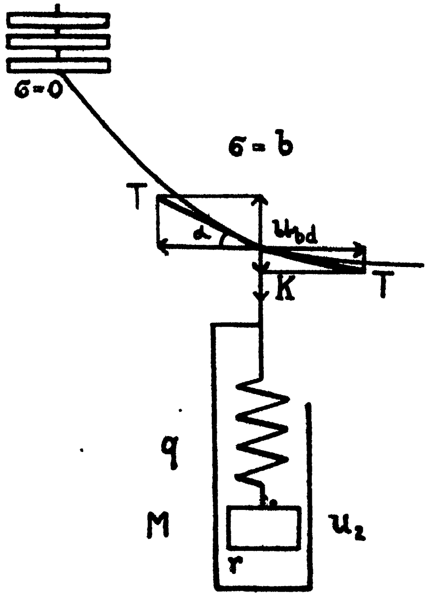

FIG. 1. *Effect of spring damper on flexible string, on the assumption that the horizontal tension is only slightly changed.*

On the assumption that the displacement u of the string varies as ϵ^{ipt}, or a sum of such terms, and in the absence of an external force ($P = 0$), the equation

$$\frac{\partial^2 u}{\partial t^2} + 2k\frac{\partial u}{\partial t} - c^2\frac{\partial^2 u}{\partial \sigma^2} = mP\epsilon^{ipt} ,$$

which applies to the string on either side of the damper, can be written (7, p. 192)

$$\frac{\partial^2 u}{\partial \sigma^2} + \frac{1}{c^2}(p^2 - 2ikp) = 0 ,$$

which has for its general solution, with

$$\begin{aligned} \lambda^2 &= (p^2 - 2ikp)/c^2 , \\ u &= (C_1 \sin \lambda\sigma + C_2 \cos \lambda\sigma)\epsilon^{ipt} , \end{aligned}$$

or a sum of such terms. The damping factor k depends in practice on the frequency. On the other hand, a particular solution of the complete equation is found in the form

$$u = C_3 \sin pt \sin \kappa\pi\sigma/s .$$

As a general solution the combination

$$u = (C_1 \sin \lambda\sigma + C_2 \cos \lambda\sigma + C_3 \sin \kappa\pi\sigma/s)\epsilon^{i(pt+\epsilon)}$$

may as usual be tried. The left-hand portion of the span between the pole and the point at which the spring is attached will have to satisfy the condition that the displacement $u = 0$ at $\sigma = 0$ (at the insulator) and $u = u_b$ at $\sigma = b$. This is the case if

$$u_L = (u_b - C_3 \sin \kappa\pi b/s)\frac{\sin \lambda\sigma}{\sin \lambda b} + C_3 \sin \kappa\pi\frac{\sigma}{s} ,$$

omitting the time function ϵ^{ipt}, since only the local amplitudes are of importance.

Similarly, for the right-hand portion of the span, $u = u_b$ for $\sigma = b$, and $u = 0$ for $\sigma = s$. This gives

$$u_R = \left(u_b - C_3 \sin \kappa\pi\frac{b}{s}\right)\frac{\sin \lambda(s - \sigma)}{\sin \lambda(s - b)} + C_3 \sin \kappa\pi\frac{\sigma}{s} .$$

At the point b, where the two sections meet, there is a slight kink in the cable owing to the weight of the mass attached to the spring, and the two equations give a different tangent. The tension thus created in the string is equal to

$$K = T\left(\frac{\partial u_L}{\partial \sigma} - \frac{\partial u_R}{\partial \sigma}\right)_{\sigma = b}$$

$$K = T\lambda\left(u_b - C_3 \sin \kappa\pi\frac{b}{s}\right)\left(\frac{\cos \lambda(s - b)}{\sin \lambda(s - b)} + \frac{\cos \lambda b}{\sin \lambda b}\right)$$

or

$$T\lambda\left(u_b - C_3 \sin \kappa\pi\frac{b}{s}\right)\frac{\sin \lambda s}{\sin \lambda b \sin \lambda(s - b)}$$

that is,

$$u_b = \frac{K}{\lambda T}\frac{\sin \lambda b}{\sin \lambda s}\sin \lambda(s - b) + \frac{C_3}{\lambda T}\sin \kappa\pi\frac{b}{s} , \text{ or a sum of such terms.}$$

In the steady state this force must be equal to that created in the spring. Taking the most general case, where a mass M attached to the spring is supposed to move in a viscous fluid contained in a cylinder carried by the wire, the force of friction being proportional to the relative velocity between string and spring weight, if (Fig. 1)

q = the spring constant, or the restoring force for 1 cm. relative displacement of the spring weight,

M = the mass suspended from the conductor, including if necessary one-third of the mass of the spring (10, p. 55),

τ = the period of the vertical oscillation of M regardless of friction,

$N = \sqrt{q/M}$ = the angular velocity at resonance, equal to $2\pi/\tau$, without damping,

$d = R/2M$ = the coefficient of damping of the spring system,

$c = \sqrt{T/m}$ = the wave velocity for transverse waves along the string,

and, if, in addition, u_2 is the displacement of the mass M of the damper from its position at rest, then (2, p. 61),

$$K = (u_2 - u_b)(q + iRp)\,,$$

while, with respect to the acceleration of M,

$$(u_2 - u_b)(q + iRp) = u_2 M p^2\,,$$

so that

$$u_2 = u_b \frac{q + iRp}{q + iRp - Mp^2}$$

and

$$K = u_b M p^2 \frac{N^2 + i2pd}{N^2 + i2pd - p^2}\,.$$

From the two expressions for K, an equation for u_b may be derived:

$$u_b = \frac{C_s \sin \kappa\pi \frac{b}{s}}{1 - \frac{Mp^2}{T} \; \frac{N^2 + 2ipd}{N^2 + 2ipd - p^2} \; \frac{\sin \lambda b \sin \lambda s\left(1 - \frac{b}{s}\right)}{\lambda \sin \lambda s}}\,.$$

By introducing this value in the equation for the left- or right-hand portion of the span, the motion of the string as influenced by the damper can be followed from point to point. It is usual, however, to suspend a damper near both ends of the span. The equation for the left-hand portion then remains the same:

$$u = \frac{u_b - C_s \sin \kappa\pi \frac{b}{s}}{\sin \lambda b} \sin \lambda\sigma + C_s \sin \kappa\pi \frac{\sigma}{s}\,,$$

whereas for the middle portion the condition that $u(\sigma) = u(-\sigma)$ and $u = u_b$ for $\sigma = b$ arises. In this case κ must be an even number and

$$u_m = \frac{u_b - C_s \sin \kappa\pi \frac{b}{s}}{\sin \lambda(s - 2b)} \left(\frac{\sin \lambda s/2}{\cos \lambda s/2} \sin \lambda\sigma + \cos \lambda\sigma\,(\sin \lambda(s - b) - \sin \lambda b)\right) + C_s \sin \kappa\pi \frac{\sigma}{s}\,.$$

The difference between the tangents to the left and right of $\sigma = b$ becomes

$$\Delta = \lambda\left(u_b - C_s \sin\frac{\kappa\pi b}{l}\right)\frac{\cos\lambda s/2}{\sin\lambda b\cos\lambda(b - s/2)} ,$$

and finally

$$u_{bd} = \frac{C_s \sin\kappa\pi\frac{b}{s}}{1 - \frac{M}{T}\frac{p^2}{\lambda}\frac{N^2 + 2ipd}{N^2 + 2ipd - p^2}\sin\lambda b\frac{\cos\lambda s\left(\frac{1}{2} - \frac{b}{s}\right)}{\cos\lambda s/2}}$$

for two dampers symmetrically placed near the ends of the span. The ratio between u_b, the undamped amplitude (for $M = 0$), and u_{bd}, the artificially damped amplitude, is, since $mc^2 = T$,

$$\frac{u_b}{u_{bd}} = 1 - \frac{M}{m}\frac{p^2}{c^2}\frac{N^2 + 2ipd}{N^2 + 2ipd - p^2}\frac{\sin\lambda b}{\lambda}\frac{\cos\lambda s\left(\frac{1}{2} - \frac{b}{s}\right)}{\cos\lambda s/2} ,$$

and should be made as large as possible. The result differs from known formulas (5) in that it takes friction into consideration.

Since b/s is much less than ½, the ratio becomes

$$\frac{u_b}{u_{bd}} = 1 - \frac{M}{T}p^2\frac{\sin\lambda b}{\lambda}\frac{N^2 + 2ipd}{N^2 + 2ipd - p^2} ,$$

regardless of whether one or two dampers symmetrically placed be used. The second damper serves to suppress the even numbered overtones.

Below critical damping, $k = p$, of the string, the fraction k/p is less than unity so that

$$\lambda = \sqrt{\frac{p^2}{c^2} - i2k\frac{p}{c^2}} \doteq \frac{p}{c} - i\frac{k}{c} ,$$

and

$$\sin\left(\frac{p}{c} - i\frac{k}{c}\right) = \sin\frac{p}{c}\cosh\frac{k}{c} - i\cos\frac{p}{c}\sinh\frac{k}{c} ;$$

the absolute value of $\sin\lambda b$ is, therefore,

$$\left|\sin\left(\frac{p}{c} - i\frac{k}{c}\right)b\right| = \sqrt{\sinh^2 k\frac{b}{c} + \sin^2 p\frac{b}{c}} = \sqrt{\frac{\cosh 2k\frac{b}{c} - \cos 2p\frac{b}{c}}{2}} .$$

The absolute value of $u_b/u_{bd} - 1$ becomes

$$\left|\frac{u_b}{u_{bd}} - 1\right| = -\frac{M}{m}\frac{p}{c}\sqrt{\frac{\cosh 2\frac{k}{p}\frac{p}{c}b - \cos 2\frac{p}{c}b}{2\left(1 + \frac{k^2}{p^2}\right)}}\sqrt{\frac{1 + \frac{4d^2}{N^2}\frac{p^2}{N^2}}{\left(1 - \frac{p^2}{N^2}\right)^2 + \frac{4d^2}{N^2}\frac{p^2}{N^2}}} ,$$

so that the influence of the string constants and that of the spring constants appear as separate factors, and may together with M/m be so adjusted that the ratio $(u_b - u_{bd})/u_{bd}$ exceeds, say 10; in this case u_b is reduced to about 9% of its former value.

Discussion of Results

It is necessary first to discuss briefly the four factors entering into the equation for $(u_b - u_{bd})/u_{bd}$.

The factor p/c increases steadily as the frequency $p/2\pi$ of the external force increases. Since, for progressive waves, the relation $p/c = 2\pi/\lambda$ holds, the ratio mc/p may be considered as $1/2\pi$ times the mass of a length of string equal to the wave-length corresponding to the frequency impressed upon the string.

The other factor referring to the constants of the conductor span, namely the difference between the hyperbolic cosine of $2kb/c$ and the ordinary cosine of $2pb/c$, is always a positive number. It is small for low frequencies, that is, small values of p/c. The largest values are obtained when b is so chosen that the ordinary cosine vanishes, that is, when $b = \lambda/8$. The distance b should therefore be shorter than half the length of the loop corresponding to the highest frequency $p = 2\pi c/\lambda$ to be expected for the most frequent wind speed.

The ratio k/p may be considered as approximately constant for a given conductor, and inversely proportional to the radius, while in reality, though only for very slow motions, it is proportional to the square root of the frequency. At the same time the value of k must be smaller than that for critical damping, $k_r = 2\kappa\pi c/s$.

The last factor in the reduction formula depends upon the frequency to which the spring damper is tuned, and, as is known from vibration engineering practice, represents the fraction of an alternating force, in the present case $u_b M p^2 \epsilon^{ipt}$, that is transmitted over a spring damper to a solid support, or from a vibrating support to the mass attached to a spring, that is, it measures the ratio, transmitted force to impressed force, or the transmissibility, D_2. When for a given coefficient of damping the impressed frequency is very low, compared to the natural frequency of the spring damper ($p < N$), the mass M completely follows the motion of the string as if it were rigidly tied to the string, and the factor becomes equal to unity. At resonance ($N = p$) the factor is equal to $(1 + p^2/4d^2)^{1/2}$ and, except when $d > N$, is therefore greater than unity. For very large values of p, on the other hand, the mass M of the damper is unable to follow the motion of the string; it remains at rest and the transmissibility is reduced to zero. While resonance is undesirable when the problem is to prevent vibrations from spreading, it is essential for reducing the vibrations of a string by means of a spring damper, and a natural frequency of the damper smaller than $1/\sqrt{2}$ times the string frequency should not be chosen. When the damper is tuned to the external frequency, the transmissibility reaches very high values so long as the damping coefficient d is small. When the damping increases to very large values, the damper is virtually prevented from moving relatively to the string, so that again it acts merely as a mass clamped to the string. While lessening the damping increases the effect upon the string, a certain amount of damping is nevertheless necessary, because the value of

$$u_2 = u_b D_2,$$

has to be kept within safe limits. Another reason for introducing damping is that in the case of the power line the damper should reduce the amplitude over a certain range of frequencies.

For each choice of d there is a frequency at which D_2 reaches its highest value. When d is a certain fraction, η, of N and $\nu = p/N$, the factor D_2 is given by

$$D_2^2 = \frac{1 + 4\eta^2\nu^2}{(1 - \nu^2)^2 + 4\eta^2\nu^2} .$$

This expression reaches a maximum for a given value of η when

$$2\eta^2\nu^4 + \nu^2 - 1 = 0 .$$

Provided that the damping is so small that the first term may be neglected, the maximum is obtained at resonance ($\nu = p/N = 1$). When the damping is appreciable, the peak lies at

$$\nu^2 = \frac{-1}{4\eta^2} \pm \frac{1}{4}\sqrt{\frac{8}{\eta^2} + \frac{1}{\eta^4}} .$$

The peak is high but narrow when friction in the damper is small; it is low and broad when there is much damping, so that the choice of the value of $2d$ depends on the range of frequencies to be suppressed. The better damping obtained for small values of $2d$ is moreover accompanied by large excursions, u_2, of the mass M of the damper which are likely to overtax the endurance of the spring.

For small values of kb/c and pb/c, the following formula holds:

$$\cosh 2kb/c - \cos 2pb/c = 2\,\frac{k^2b^2}{c^2} + 2\,\frac{p^2b^2}{c^2} = 2\,\frac{b^2}{c^2}\,p^2\left(1 + \frac{k^2}{p^2}\right) ,$$

so that

$$\frac{u_b}{u_{bd}} - 1 \qquad \frac{M}{m}\;\frac{p^2b}{c^2}\sqrt{\frac{1 + \frac{4d^2}{N^2}\;\frac{p^2}{N^2}}{\left(1 - \frac{p^2}{N^2}\right)^2 + \frac{4d^2}{N^2}\;\frac{p^2}{N^2}}} = -\frac{M}{T}\,bp^2\sqrt{\frac{1 + 4\eta^2\nu^2}{(1 - \nu^2)^2 + 4\eta^2\nu^2}} ,$$

and it seems safe to use this formula, which does not depend on the damping of the string, in most practical cases.

The following example illustrates the relative influence of the various factors. A damper is to be designed for a stranded aluminium conductor of No. 00 B. & S. gauge (0.414 in. diameter, or about 1.2 cm.) suspended between two fixed points at the same elevation, 160 metres (480 ft.) apart and so strung that the maximum stress does not exceed 14,000 lb. per sq. in. with a combined load of 0.5 in. ice coating and a 47-mile-an-hour wind (5 lb. pressure per sq. ft.) at −20° F. The sag without this load at the centre of the span is then 16.5 ft. at −14° F., 18 ft. at 34° F. and 19.7 ft. at 90° F., the total tension varying between about 220 and 183 lb. (9, p. 123). The weight per foot of conductor is 0.125 lb.; therefore c is about 210 ft. per sec. (or 6280 cm. per sec.) at the highest temperature. If the average wind velocity is from three to four miles per hour, frequencies of about 30 cycles per second will be strongly excited; their wave-length is about seven feet ($\lambda/8 = 26$ cm.). The fundamental frequency of the span is about one-half cycle per second.

The influence of the factors p/c, $\sin \lambda/\lambda$ and of the damper D_2 (for which $2d$ has been assumed to be equal to 10, while $N_2 = 25$, making the damping critical for $d = 25$) may be seen from Table I. By computing the value of

TABLE I

EFFECT OF TUNED DAMPER ON VIBRATING STRING

($c = 2000\pi$ cm. per sec.)

Resonance frequency, 25 cycles per sec., $d/d_{cr} = 0.032$

f	$2\pi f = p$	p/c	D_2		$b = 10$ cm.		$b = 20$ cm.	
			$2d_2 = 50$	$2d_2 = 10$	$\frac{c}{p}\ \frac{\sin\lambda}{\lambda}$	$\left(\frac{u_b}{u_{bd}} - 1\right)\frac{m}{M}$	$\frac{c}{p}\ \frac{\sin\lambda}{\lambda}$	$\left(\frac{u_b}{u_{bd}} - 1\right)\frac{m}{M}$
0.5	π	0.0005	1.00	1.00	0.005	0.000	0.01	0.000
1	2π	0.001	1.00	1.00	0.010	0 000	0.02	0.000
5	10π	0.005	1.01	1.00	0 05	0.000	0.10	0.0005
10	20π	0.010	1.16	1 19	0.10	0.001	0.20	0.002
15	30π	0.015	1.25	1.65	0 15	0.004	0.30	0.007
20	40π	0.020	1.45	2.57	0.20	0.010	0.39	0.020
21	42π	0.021	1.49	2.85	0.21	0.012	0.41	0.025
22	44π	0 022	1.47	3.05	0.22	0.015	0.43	0.029
23	46π	0.023	1.47	4.23	0.23	0.022	0.44	0.043
24	48π	0 024	1.43	4.86	0.24	0.028	0.46	0.054
25	50π	0.025	1.41	5.00	0.25	0.031	0.48	0.060
26	52π	0 026	1.38	4 52	0.26	0.030	0.50	0.059
27	54π	0.027	1 35	3 80	0 27	0.028	0.51	0.052
28	56π	0 028	1 32	3 16	0.28	0.025	0.53	0.048
29	58π	0 029	1 26	2 39	0.29	0 020	0.55	0.038
30	60π	0 030	1 18	1 87	0 30	0 017	0.57	0.033
35	70π	0.035	1 02	2 90	0.34	0.011	0.64	0.021
40	80π	0 040	0 7	0 56	0.39	0.009	0.72	0.016

Damping is satisfactory over a band of about five cycles on each side of the resonance frequency N_2.

$\sin \lambda/\lambda$ for two distinct values of natural damping of the cable, namely 0 and 0.25 for the resonance frequency, varying as the square root of the frequency, it is shown that within these limits natural damping produces relatively little effect, and the final results refers to the absence of friction. The contribution of the damper for $M/m = 1$ is several times larger, but the value of c in p/c is responsible for a low total reduction. In order to bring the amplitude down to about 10% of the original displacement at $\sigma = b$, it is therefore necessary to give M/m a value of several hundred units, that is, to make the mass of the damper equal to the mass of a length of cable about equal to the wave-length of the frequency to be damped ($\lambda = 2\pi c/p$). Dampers of this kind have been found in many tests to completely suppress the vibrations of the cable (5).

As a second example, a 500,000 circular-mil stranded copper cable (diameter 0.813 in., weight 1.54 lb. per ft.) may be discussed. The elastic limit is 28,350 lb. per sq. in.; the maximum allowable tension, 75% of the elastic limit, is about 8350 lb. when the ice is 0.5 in. thick (0.8 lb. per ft.); and the wind pressure 10 lb. per sq. ft. (wind load 1.5 lb. per ft.). As the tower spacing is varied from 300 to 1200 ft.(90 to 360 metres), the permissible tension without wind and ice varies between 3620 lb. at 100° F. and 6800 lb. at −10° F. for the 300 ft. span, and between 4500 lb. (at 100° F.) and 4750 lb. (at −10 °F.) for the 1200 ft. span (9, p. 205). The velocity of propagation, c, for the 1200 ft. span is therefore between 310 and 320 ft. per sec. or at the most 3000 π cm. per sec., while for the 300-ft. span it varies between 1275 ft. per sec. (8250 cm. per sec.) at the highest temperature and nearly 363 ft. per sec. (10,890 or 3500 π cm. per sec.) at the lowest temperature (3, p. 205).

The main change with respect to the first example is the change of the wave velocity from 2000 π to 3000 π cm. per sec., resulting in shorter loops for standing waves of the same frequency, while, on account of the doubled diameter, winds of the same speed now produce correspondingly lower frequencies. The value of p/c is reduced by about one-third, the value of the factor $\sin \lambda/\lambda + pb/c$ is reduced in that k is smaller for larger diameters, while b, on account of the larger value of c, will have to be increased so that it may offset the change in p/c. The damper has to be tuned to 12.5 cycles per second in place of the former value of 25 cycles. If the same damper were used it would produce only about one-third or one-fourth as much effect as it would on the line for which it had been designed.

Application of the Theory of Damping

While given for a definite form of damper used to some extent on power lines (4, 5), namely, a spring with a heavy mass attached to one end and viscous damping proportional to the velocity of the mass with respect to the support, the theory is readily adapted to various simpler types of actual or possible dampers. It is merely necessary to insert the proper value for the force K exerted at the suspension point. In the tuned damper itself the spring may be replaced by a piece of rubber with high internal friction.

When frictional forces proportional to the velocity of the mass of the damper are used, as in air damping or electric damping,

$$K = u_2 M p^2 = i u_2 R p + (u_2 - u_b)(q + iRp)$$

or

$$K = u_b M p^2 \frac{N^2}{N^2 + i2pd - p^2}$$

so that the only change with respect to the damper discussed before, in which friction is proportional to the relative velocity between damper and string, is the suppression of the term $i2pd$ in the numerator of D_2. With the amount of damping used in practice the difference is slight.

Vibrating rods or blades attached to the conductor with or without masses fastened to them are thus but a special form of the spring damper. In the simplest case a steel blade l cm. long, w cm. wide and h cm. thick may be clamped with one end at some point along the span, and a mass M fastened to the other end of the blade (Fig. 2-I). When the vibrations are so small

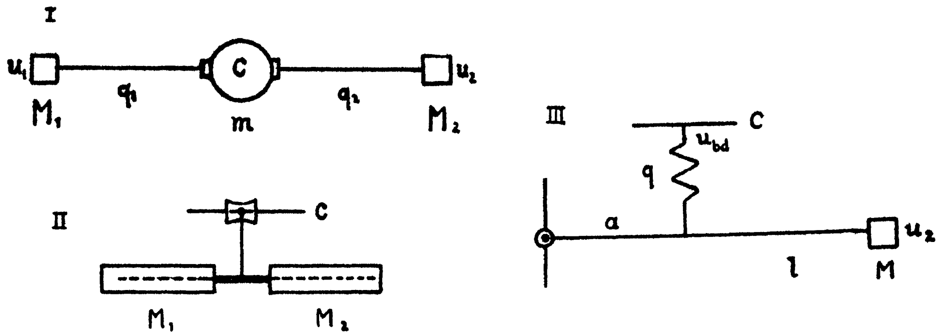

FIG. 2. *Various devices based on the principle of the tuned spring damper. In I, thin cantilevers serve for tuning in place of springs. II is the widely used Stockbridge damper, the over-all length being about 50 cm. and M_1 and M_2 each weighing 3 to 4 kg.*

that the mass moves sensibly up and down only, a force P at the free end of the cantilever gives a deflection $u_2 = Pl^3/3EI$, where E is Young's modulus of elasticity and I the moment of inertia of the cantilever, namely, $bh^3/12$ for vibrations taking place in the stiffer cross-section and $bh^3/48$ for vibrations taking place in the more flexible cross-section. The spring constant is therefore

$$q = P/u_2 = 3EI/l^3 .$$

When the loaded blade is replaced by a cylindrical bar or cable (4, 8), as is the case in the Stockbridge damper, $I = \pi d^4/64$. Apart from the different meaning of the elastic constant, the theory of this damper (Fig. 2-II) is the same as that of the tuned spring damper. At the limit the damper becomes simply a rod or strip of metal of length of about one loop attached to the cable and vibrating in its natural frequencies (4, 8).

In some cases it may be possible to fasten one end of the cantilever to a pin on the mast, and to let the mass act with the lever arm l on the spring suspension (Fig. 2-III). The effective spring constant is changed to aq/l.

Broadening of Resonance Through Coupling

By choosing dampers tuned to the different frequencies, damping is obtained over a wider range of frequencies. A broadening of the response of the damper is also due to the fact that the vibrating mass of the conductor effects a coupling between the dampers, whether these are used side by side or are symmetrically placed near the two ends (Fig. 2-I). If m_3 designates a vibrating mass representing the string, m_1 and m_2 and q_1 and q_2 the mass and spring constants of the dampers, and u_1, u_2 and u_3 the displacements, the equations

$$\begin{aligned} m_1\ddot{u}_1 + k_1(u_1 - u_2) &= 0 \\ m_2\ddot{u}_2 + k_1(u_3 - u_2) &= 0 \\ m_3\ddot{u}_3 + k_1(u_1 - u_3) + k_2(u_3 - u_2) &= 0 , \end{aligned}$$

hold for longitudinal or small transverse motions, and the angular resonance frequencies are given by

$$N^4 - N^2\left(k_1 \frac{(m_1 + m_3)}{m_1 m_3} + k_2\left(\frac{m_2 + m_3}{m_2 m_3}\right)\right) + \frac{m_1 + m_2 + m_3}{m_1 m_2 m_3} = 0 .$$

When m_3 is larger than either m_1 or m_2, the two solutions are

$$N^2 = \tfrac{1}{2}\left(\frac{k_1}{m_1} + \frac{k_2}{m_2}\right) \pm \sqrt{\tfrac{1}{4}\left(\frac{k_1}{m_1} - \frac{k_2}{m_2}\right)^2 + \frac{m_1 m_2}{m_3^2}\,\frac{k_1}{m_1}\,\frac{k_2}{m_2}}\,.$$

or, writing N_1 for k_1/m_1 and N_2 for k_2/m_2

$$N^2 = \tfrac{1}{2}(N_1 + N_2) \pm \sqrt{\tfrac{1}{4}(N_1 - N_2)^2 + \frac{m_1 m_2}{m_3^2} N_1 N_2}\,.$$

Coupling of the dampers through the conductor, therefore, lowers the frequency of the damper with the lower frequency, and increases the frequency of the damper tuned to the higher frequency. If the two frequencies are not too far apart, the entire band between them is reduced in amplitude.

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THE INFLUENCE OF A MAGNETIC FIELD ON THE DIELECTRIC CONSTANTS OF GASEOUS AND LIQUID NITROGEN AND OXYGEN[1]

BY ALLAN C. YOUNG[2]

Abstract

The results of an experimental determination of the effect of a magnetic field on the dielectric constants of gaseous and liquid oxygen and nitrogen are given. With the gases a balanced resonance method was used, and with the liquids, a special bridge. The only positive result obtained was with gaseous oxygen at a pressure of 100 atm., and this can be accounted for quantitatively by the increased pressure of the oxygen in the magnetic field.

Introduction

The effect of a magnetic field on the dielectric constant, or more exactly the electric susceptibility of gases, is a problem of considerable interest, in the classical theory and new quantum mechanics, on account of its relation to the anisotropy of the molecules, and, in the old quantum theory, as a test of the validity of the spatial quantization of the angular momentum of the molecule in an applied field. The magnitude of the effect on the classical theory has been calculated by Weigle (9) and Van Vleck (4, 5, 6), and that on the old quantum theory by Pauling. The calculation of the effect on the new quantum mechanics has been attempted by Niessen (2), but his results hold only for a very specialized type of molecule which apparently has little physical significance. His results for this type of molecule agree in order of magnitude with calculations according to classical theory. More exact calculations have not been made, owing to mathematical difficulties and lack of experimental data. A complete outline of the problem and its theoretical significance is given by Van Vleck.

Several investigators, notably Weatherby and Wolf (8), Mott-Smith and Daily (1), Pützer (3), and Voss (7), have studied experimentally the effect of a magnetic field on the dielectric constant of gases. They found that within their limit of error, which in the case of Pützer and Voss was about one part in ten million, and more for the others, a magnetic field had no effect on the dielectric constant.

Weatherby and Wolf used a heterodyne method to measure the capacity change. They counted the number of beats produced per second between two oscillators, one with a fixed frequency and the other having a test con-

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denser filled with the gas under test in its load circuit. They estimate that they can measure a frequency change of one cycle per second, which with their apparatus corresponds to a capacity change of one part in five hundred thousand. Mott-Smith and Daily used a similar method but measured their capacity change by observation of the change in the Lissajous figures produced by the superposition of the frequencies of the two oscillators. They estimate that they can detect a capacity change of one part in a hundred thousand. Pützer, using a method fundamentally the same as the latter, claims a sensitivity 100 times as great as that reported by Mott-Smith and Daily. In the apparatus used by Voss a test condenser formed part of a resonant circuit excited by a vacuum tube oscillator. The capacity and inductance values in the resonant circuit were adjusted to give the maximum current change in the resonant circuit for a given small capacity change. This current was passed through a thermocouple and the resulting direct current balanced against the current from another thermocouple also coupled to the oscillator. Since the calibrations of the two thermocouples were nearly the same, small changes in the oscillator intensity should not have affected the balance. The change of the balance current gave a measure of the change of capacity in the test circuit. For small capacity changes, the current change was directly proportional to the capacity change; with a very sensitive galvanometer in his balance circuit, Voss claims to have been able to detect capacity changes of one part in a hundred million. He did not, however, give this figure as his final limit of error, nor did he calibrate his apparatus in units of this order.

All these methods have one serious disadvantage, inasmuch as they depend on the condition that there be no circuit variations other than capacity change. The frequency stability of any ordinary oscillator is not much better than one part in a hundred thousand for a carefully designed oscillator. The frequency variations are probably due mainly to battery changes and surface charges on the glass of the vacuum tubes. In Voss's method this could be overcome by using a quartz crystal oscillator which has a possible deviation of one part in a million, or even in ten million for a circuit with thermostatic control. Temperature changes in the condenser itself constitute another source of error, changes of one-tenth of a degree cause a change of capacity of about one part in a million. A third source of error is the change of pressure of the gas in a magnetic field, an effect that depends on the magnetic susceptibility of the gas.

Experimental

In the present investigation both the heterodyne method and a modification of Voss's method were tried with gases. The detectable capacity change with the heterodyne method was found to be about one part in a hundred thousand; with the resonance method, about one-tenth of this. Hence, the modification of Voss's method shown in Fig. 1 was adopted for use with gases at high pressure. The vacuum tubes in the balance circuit were 8 ft. from the magnet, and were not appreciably affected by the magnetic field. Details of the layout and the test condenser are given in Figs. 2 and 3.

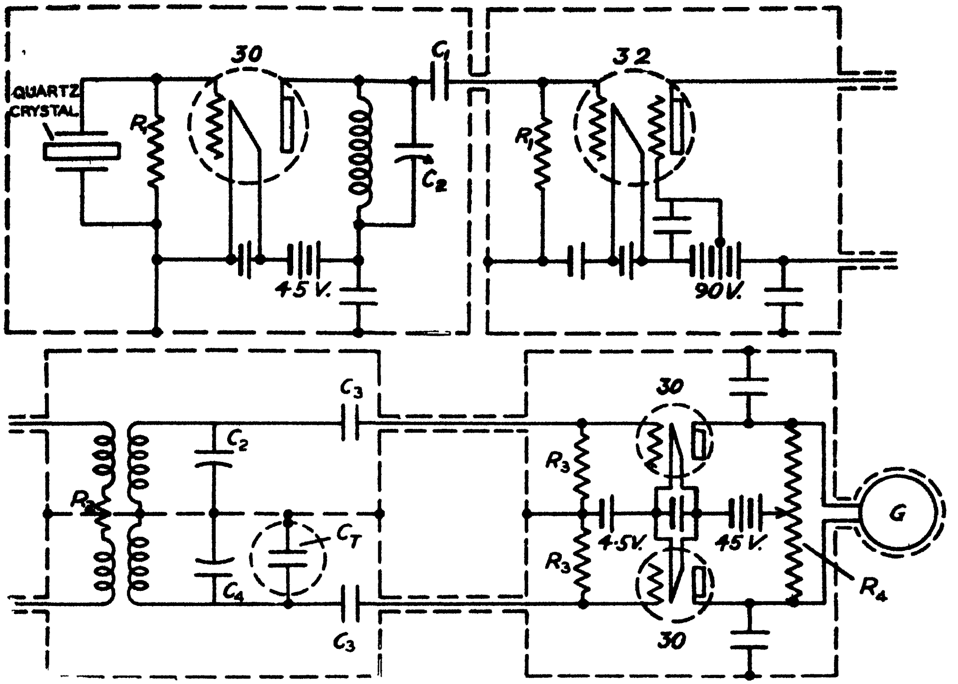

FIG. 1. *Variation of Voss's method for dielectric constant.* R_1 = *2 megohms,* R_2 = *50.000 ohms,* R_3 = *1 megohm,* R_4 = *10,000 ohm potentiometer,* C_1 = *20* $\mu\mu f$.*,* C_2 = *50* $\mu\mu f$. *max. V C.,* C_3 = *10* $\mu\mu f$. *max. V.C.,* C_4 = *2.5* $\mu\mu f$. *max. V.C., with a calibration of 3.5* × 10^{-4} $\mu\mu f$. *per scale division,* C_T = *test condenser. All by-pass condensers are 0.1* μf. *G = galvanometer.*

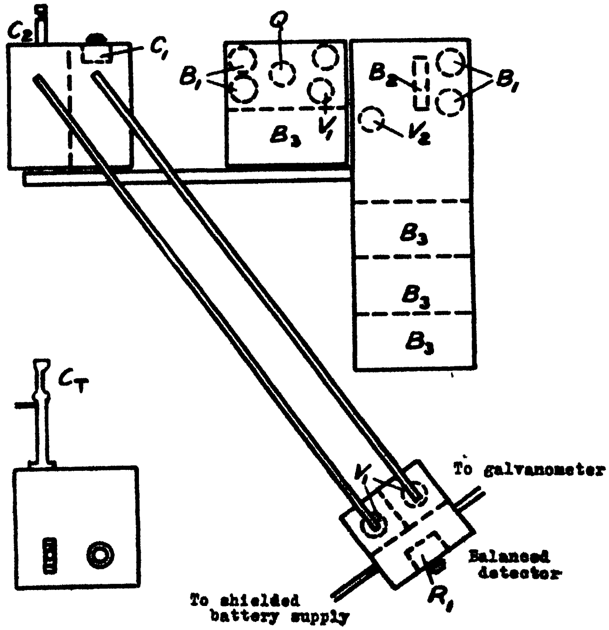

FIG. 2. *Actual layout of apparatus in 1.* B_1 = *1.5 volt dry cell,* B_2 = *4.5 volt dry battery,* B_3 = *45 volt dry battery,* C_1 = *50* $\mu\mu f$. *max V.C.,* C_2 = *2.5* $\mu\mu f$. *max. V.C.,* C_T = *test condenser,* Q = *quartz crystal,* R_1 = *10,000 ohm wire-wound potentiometer,* V_1 = *Type 30 tube,* V_2 = *Type 32 tube.*

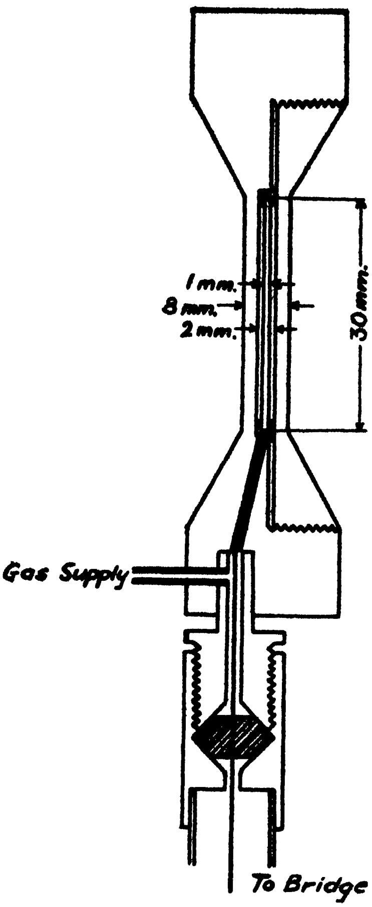

FIG. 3. *Detail diagram of test condenser for gases.*

The plate current of the vacuum tubes could be balanced to 10^{-9} amp. with no high frequency voltage on the grid, but only to 10^{-8} amp. when the circuit was used with the high-frequency voltage applied to the grids. With this circuit a change of one scale division on the vernier condenser, corresponding to a capacity change of 3.5×10^{-4} $\mu\mu$f., caused a current of 1.8×10^{-7} amp. to flow through the galvanometer. This places a limit of 2.0×10^{-5} $\mu\mu$f. on the detectable capacity change. With the test condenser used, which had a capacity of 25 $\mu\mu$f., the minimum observable change in dielectric constant would be one part in 1.2×10^6. This method was not satisfactory for use with liquid oxygen or nitrogen, chiefly because of variations in capacity caused by temperature changes in the leads to the condenser.

For this reason the circuit used with liquids was a specially designed bridge in which variations due to temperature changes were nearly eliminated (Fig. 4). The practicable sensitivity of this bridge was less than that of the previous apparatus at room temperatures, but with liquids at low temperature the sensitivity was greater. With liquid oxygen and nitrogen in the condensers, a change of capacity of one part in a hundred thousand could be measured.

The bridge circuit can be considered as consisting of three distinct units, the feeding circuits, the bridge proper and the null indicator for determining the balance of the bridge. The feeding circuit consisted of a crystal oscillator (frequency 2.1 megacycles per second) and an amplifier connected to the input transformer of the bridge. The primary and secondary of the input transformer were shielded electrostatically from each other. The layout of the apparatus is shown in Fig. 5.

The bridge proper is made as symmetrical as possible in all respects. Two arms of the bridge consist of 50-$\mu\mu$f. maximum variable air condensers enclosed in a heavy copper shield connected to one side of each condenser. This shield prevents any variation of the capacity of the two condensers to ground when they are being adjusted. The other two arms of the bridge are condensers containing the liquid to be measured and a 200,000 ohm variable resistance. As may be seen from the diagram (Fig. 4) the input coil may also be considered as part of these arms, and any dissymmetry in

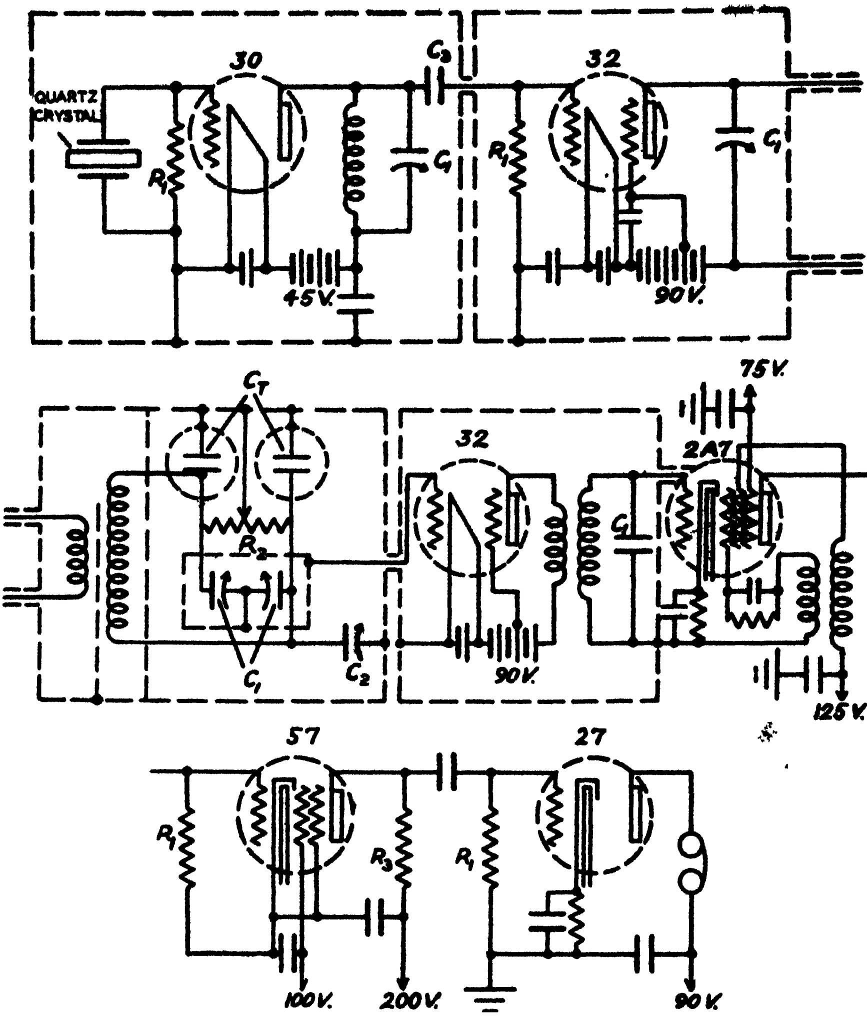

FIG. 4. *Diagram of apparatus used for the investigation of the effect of a magnetic field on the dielectric constants of liquid oxygen and nitrogen.* R_1 *= 2 megohms,* R_2 *= 200,000 ohm wire-wound potentiometer,* R_3 *= 100,000 ohms,* C_1 *= 50 μμf. max. V.C.,* C_2 *= 2.5 μμf. max. V.C. calibration of 3.5 × 10^{-4} μμf. per scale division,* C_3 *= 20 μμf.,* C_T *= test condenser. All by-pass condensers are 0.1 μf.*

it will affect the resistance balance of the two arms. The variable resistance is adjusted to balance these resistances and any others that may be present owing to the resistance of the leads and dielectric losses. The design of the test condensers is shown in Fig. 6. The plates are made as nearly as possible identical. The double-walled container is designed to prevent any bending of the inner container by pressure effects developed by the magnetic field. A small variable condenser is connected in parallel with one of these condensers, and is used for the final balancing of the bridge and for measuring any change of dielectric constant.

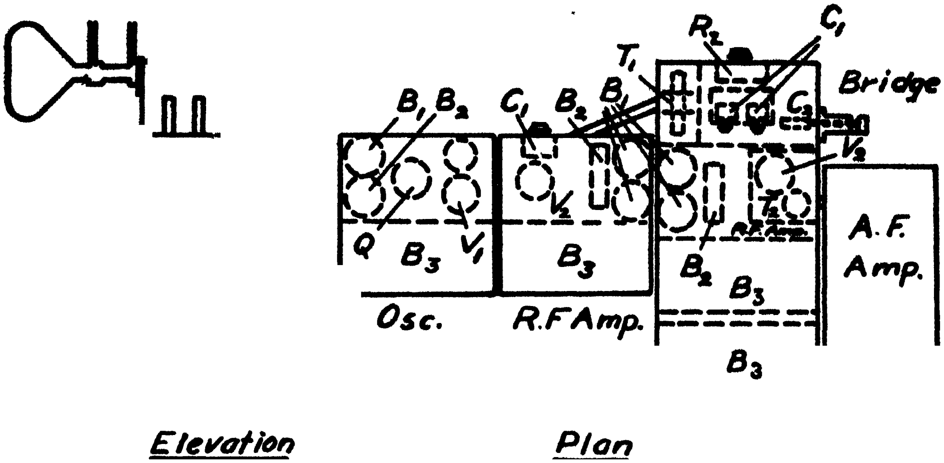

FIG. 5. *Layout of apparatus in Fig. 4.* B_1 = *1.5 volt dry cell,* B_2 = *4.5 volt dry battery,* B_3 = *45 volt dry battery,* C_1 = *50 μμf. max. V.C.,* C_2 = *2.5 μμf. max V.C.,* R_2 = *200,000 ohm wire-wound potentiometer,* T_1 = *input transformer to the bridge,* T_2 = *output transformer to the converter tube,* V_1 = *Type 30 tube,* V_2 = *Type 32 tube,* Q = *quartz crystal.*

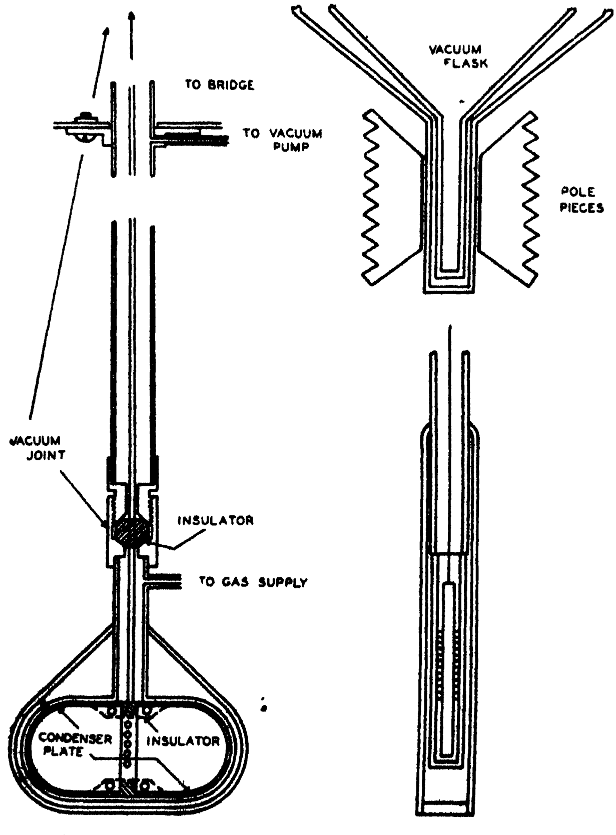

FIG. 6. *Detail diagram of vacuum flask condenser for liquids.*

The output circuit is connected to the shield of the two variable condensers and to ground, which is the common point of the two fixed condensers. The current from the bridge is passed through a one stage, shielded, high-frequency amplifier to a converter tube. In this tube the current from the bridge is mixed with a current of slightly different frequency generated in the converter tube. These two currents combine to give in the output of the tube a current whose frequency is the difference of frequencies generated by the crystal oscillator and converter tube. This current, which has a frequency of a few thousand cycles per second, is further amplified and then fed to a pair of earphones. This method was adopted as it is more sensitive for small currents (*i.e.*, when the bridge is near balance) than the more customary method of modulating the oscillator output and using an audio frequency amplifier as a balance detector.

The test condenser and its replica are mounted in a specially made German silver Dewar flask. This flask has an external width of only 13 mm. in the vicinity of the test condenser. This permits the placing of the pole pieces of the magnet less than 15 mm. apart. The magnet is a standard Boas electromagnet which, with a current of 22 amp., has a field strength of 19,000 gauss over an area of 7 sq. cm. when the gap is 15 mm. The field strength was measured with a bismuth spiral. Both types of apparatus were tested by observing the effect of the magnetic field when the test condensers were evacuated to a pressure of 0.01 mm. of mercury. No effect was observed within the stated limits of error.

All previous workers have used gases at atmospheric pressure or less. However, classical theory predicts that the electrical susceptibility, χ, of a gas in a magnetic field, H, will be (6, p. 117)

$$\begin{aligned}\chi &= N(a + bH^2)\\ &= \chi_0(1 + b/aH^2)\ ,\end{aligned}$$

where N is the number of molecules per cc.

$$a = \frac{\mu_1^2 + \mu_2^2 + \mu_3^2}{3kT} + \frac{\alpha_{11} + \alpha_{22} + \alpha_{33}}{2}$$

$$b = \frac{3\cos^2\Psi - 1}{90k^2T^2} \sum_{i>j} \left[(\mu_i^{*2} - \mu_j^{*2})\left(\frac{\mu_i^2 - \mu_j^2}{kT} + \alpha_{ii} - \alpha_{jj}\right) + 6\mu_i^* \mu_j^* \left(\frac{\mu_i \mu_j}{kT} + \alpha_{ij}\right)\right]$$

where μ_1, μ_2, μ_3 are the components of permanent electric moment of the molecule, μ_1^*, μ_2^*, μ_3^* are the components of permanent magnetic moment of the molecule, α_{ij} are the polarization coefficients and are a measure of the distortion of the molecule by an applied electric field; i and j can take the values 1, 2, 3. ψ is the angle between the applied electric and magnetic fields.

From this it follows that the dielectric constant, ϵ, is given by:

$$\epsilon = 1 + 4\pi\chi_0(1 + bH^2/a)\,.$$

Therefore $\frac{\Delta\epsilon}{\epsilon_0} \doteq cH^2\{\chi_0/(1 + 4\pi\chi_0)\}/T^2$, where $\Delta\epsilon = \epsilon_H - \epsilon_0$, (1)

since the μ's are all zero, as oxygen and nitrogen are non-polar (*cf.* Van Vleck (4,5,6)).

Using this classical result as a guide, it follows that the percentage change in dielectric constant, for a given magnetic field, will be increased by an increase in χ_0 and a decrease in temperature. Hence measurements of the effect of a magnetic field on the dielectric constant of oxygen and nitrogen were made under the following conditions:

1. At 100 atm. pressure and room temperature.
2. In the liquid state at the temperature of liquid air under atmospheric pressure.

While these conditions are such that Equation (1) would not be expected to hold exactly, nevertheless it is unlikely that the order of magnitude of the effect would be changed.

Results

In the preliminary work, in which a method similar to that employed by Voss was used, an apparent increase of the dielectric constant of oxygen gas at 100 atm. pressure and room temperature was observed. The balance current changed by 1.4×10^{-8} amp., which corresponds to a change of 1.1×10^{-6} in the dielectric constant. With nitrogen gas under similar conditions no effect was observed. The change in the capacity however may be attributed to the pressure change in the gas in the condenser due to the applied field. If K is the volume-magnetic susceptibility of the gas, the pressure increase will be:

$$\Delta p = KH^2/2 \ ;$$

for oxygen at 20° C. and 100 atm.

$$K = 1.4 \times 10^{-5}$$

$$\therefore \Delta p = 1.9 \text{ mm. of mercury.}$$

Since the dielectric constant of oxygen at 20° C. and one atmosphere is 1.00051, the change in dielectric constant will be

$$\Delta\epsilon = 1.3 \times 10^{-6} \ .$$

This is the value observed, within experimental error. The magnitude of the magnetic susceptibility of nitrogen is only $\frac{1}{300}$ that of oxygen, hence no effect is to be expected due to pressure changes. Since the compressibility of liquids is much less than that of gases, this magnetic effect will not introduce errors of so large a magnitude in the measurements of their electric susceptibilities. Based on calculations similar to the above, the change in the dielectric constant of liquid oxygen is approximately one part in a million for a field of 20,000 gauss.

With the bridge previously described no change was observed in the dielectric constant of liquid oxygen or nitrogen in fields as strong as 19,000 gauss. Since the only effect observed is that on oxygen gas at high pressure and in strong magnetic fields, and since this effect may be accounted for by the increase of pressure of the gas in the magnetic field, it may be concluded that any effect of magnetic field on the dielectric constant is at least as small as that indicated by rough calculations based on the classical theory. Further it may be concluded that any effect on oxygen at least will be masked by the presence of magnetostrictive effects which, with apparatus of the type described, cannot be calculated exactly owing to field inhomogeneities.

TABLE I

LIMIT OF ERROR IN WORK BY PREVIOUS INVESTIGATORS

Gas	Author	$\Delta\epsilon/\epsilon$	$\Delta\chi/\chi$	$T^2\Delta\chi/H^2\chi$
He	Weatherby and Wolf	2×10^{-6}	1×10^{-1}	1×10^{-4}
O_2	Weatherby and Wolf	2×10^{-6}	4×10^{-3}	5×10^{-8}
NO	Mott-Smith and Daily	1×10^{-5}	8×10^{-2}	3×10^{-4}
HCl	Mott-Smith and Daily	1×10^{-5}	1×10^{-3}	3×10^{-5}
N_2	Pützer	1×10^{-7}	2×10^{-4}	2×10^{-7}
O_2	Pützer	1×10^{-7}	2×10^{-4}	2×10^{-7}
O_2	Voss	3×10^{-7}	1×10^{-3}	1×10^{-4}
A	Voss	5×10^{-7}	1×10^{-3}	7×10^{-5}
O_2	Young	1×10^{-8}	2×10^{-3}	4×10^{-9}
N_2	Young	1×10^{-8}	2×10^{-5}	4×10^{-9}
O_2 (liquid)	Young	1×10^{-5}	3×10^{-5}	6×10^{-10}
N_2 (liquid)	Young	1×10^{-5}	3×10^{-5}	6×10^{-10}

Acknowledgments

The author wishes to acknowledge his indebtedness to Dr. E. F. Burton, Director of the laboratory, and to Mr. A. Pitt for their advice and assistance.

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STUDIES ON EXPLOSIVE ANTIMONY

III. THE MAGNETIC SUSCEPTIBILITY[1]

By C. C. Coffin[2]

Abstract

Explosive antimony is not as diamagnetic as the ordinary polycrystalline metal. The magnetic susceptibilities are respectively -0.38×10^{-6} and $-0\ 88 \times 10^{-6}$. The explosive or amorphous form should therefore be regarded as a true glass of the supercooled liquid. The fact that it is less "metallic" than the molten metal cannot be the result of the metallic binding of the liquid or crystalline state changing to homopolar binding in the amorphous state.

Introduction

The data presented in Parts I (4) and II (3) of this series indicate that explosive antimony is amorphous, and that its "explosion" is a crystallization. The properties of this unstable electrolytic deposit are being studied in the hope that they may throw some light on the problem of amorphous metals in general. It seems probable that no other metal can be obtained in the amorphous state so easily and in such quantities.

Measurements of the magnetic susceptibility were undertaken with the object of determining the type of atomic binding characteristic of the amorphous metal. Ordinary crystalline antimony and bismuth are diamagnetic because of the presence of homopolar bonds. The disappearance of these bonds when the crystal melts is accompanied by a decrease in diamagnetism and electrical resistance, so that the liquid is more truly a metal than is the solid. If explosive antimony is amorphous in the sense that it is a glass of supercooled liquid, it should therefore be less diamagnetic than ordinary antimony.

On the other hand, the electrical properties indicate that explosive antimony is far less metallic than crystalline antimony (3). If this loss of metallic properties is the result of the replacement of metallic by homopolar binding, explosive antimony should be even more diamagnetic than the crystalline variety. Bernal has pointed out that the structure of the latter can be pictured as a layer lattice in which the bonds between the atoms of a layer are homopolar, and those between the layers are metallic (1, p. 375). In keeping with this view is the fact that crystalline antimony has a higher conductivity across than in the cleavage plane, and shows directional abnormalities in the conductivity at high pressures (2, p. 274). In explosive antimony, cleavage planes and, to a large extent, metallic properties have disappeared, so that it seems not unreasonable to suspect that the metallic bonds of the ordinary metal have become homopolar in the amorphous form.

[1] *Manuscript received November 4, 1935.*
Contribution from the Laboratory of Physical Chemistry, Dalhousie University, Halifax, N.S., Canada. The data reported in this paper were included in a communication to the Royal Society of Canada at Hamilton, Ont., June 1935.

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The determination of the magnetic susceptibility of the explosive deposit offers an obvious means of choosing between these two possibilities. It may be stated at once that the amorphous metal is much less diamagnetic than the polycrystalline metal, so that in all probability the former is a true glass of the supercooled liquid.

Experimental

Preparation of Specimens

Fairly large cylindrical specimens of uniform composition and cross section were required for the magnetic susceptibility measurements, which were made by a modified Gouy method. As the material cannot be machined without explosion the specimens used were untouched electrolytic deposits. It has been already shown (4, 5) that the chemical and physical uniformity of an explosive cathode depends largely upon the efficiency with which the bath is stirred during the deposition. A poorly stirred bath will yield rough and misshapen cathodes which often consist of a mixture of the explosive and non-explosive forms. Such deposits are coarsely botryoidal in structure and have little or no metallic lustre. High speed stirring, on the other hand, results in symmetrical deposits of uniform chemical composition. If a cathode be rapidly rotated about its own axis in a well stirred bath, the finished product will generally resemble a rod of highly polished steel.

The stirring arrangement shown in Fig. 1 proved to be very satisfactory. A large gear, *A*, 9 cm. in diameter, is fixed to the stationary shaft, *B*, which supports the whole mechanism. A small gear, *C*, is carried on either end of the bar *D* which is fixed to the driving pulley, *F*, by a hollow shaft, *H*. The copper wire cathodes are held in chucks attached to the gears, *C*, which mesh with *A* and therefore rotate about their own axis as they revolve with *D*. The gear ratios are such that the smaller two make five revolutions about their own axis for every revolution about *A*. The cross bar, *D*, was turned at the rate of 300 r.p.m. The anode of cast chemically pure antimony was mounted at the centre of the electrolysis cell as shown in the figure. The electrolyte was redistilled chemically pure antimony trichloride dissolved in 10% hydrochloric acid solution. Precautions were taken to avoid contamination by iron.

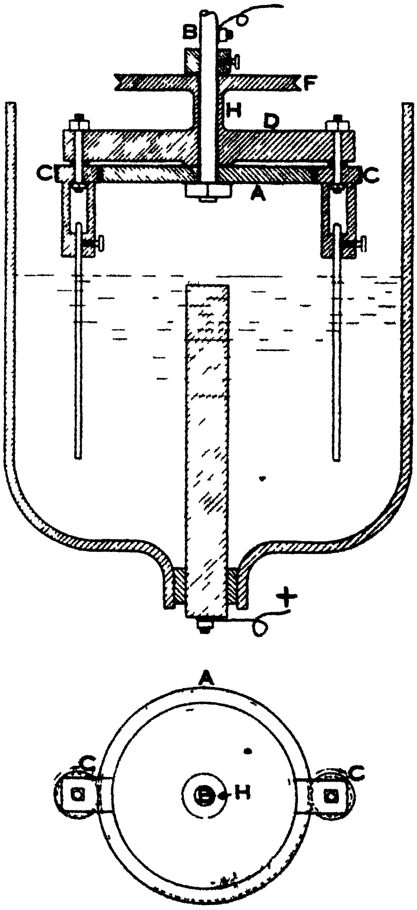

Fig. 1. *Details of cathode-stirrer.*

Although very uniform specimens could be prepared with this apparatus, it proved to be unexpectedly difficult to make them very large. On attaining a certain size (less than 1 cm. in diameter) the cathodes usually exploded in the bath unless the current density was kept so low that the deposition proceeded at an inconveniently slow rate. The explanation of these explosions is probably to be found in the fact that the amorphous metal has a very high resistance (4), which at high current densities might lead to local heating above the temperature (about 100° C.) at which the crystallization becomes explosive. After many attempts three suitable specimens were obtained in non-stop runs of 30 to 40 hr. duration.

Magnetic Susceptibility Measurements

The specimen was carried in a light, close-fitting test tube suspended by a fine copper wire from the beam of an analytical balance, which stood on a firm support about two feet above the flat-faced pole pieces of a large electromagnet. The length of the copper wire was such that the lower end of the specimen was about 1 cm. below the top of the pole pieces, which were spaced with hardwood blocks to form a gap not more than 1 mm. greater than the diameter of the glass tube. The susceptibility of a specimen was determined by comparing the apparent change in weight caused by the field with the change that the same field produced in the apparent weight of the glass tube filled with distilled water. Corrections must be made for the diamagnetism of the glass and of the copper wire (the cathode basis metal) embedded in the antimony specimen, as well as for the fact that the cross section of the water column is necessarily greater than that of the antimony. The method of making these corrections will be clear from the following sample calculation. The density of explosive antimony is taken as 6.8 and the magnetic susceptibility of water as -0.72×10^{-6}.

Sample Calculation

Experiment 12, Specimen 3. Temperature 25–27° C.

	Current in magnet, amp.	Weight (W), gm.	ΔW
Glass tube + copper wire	0	4.5442	
	3.000	4.5402	−0.0040
Glass tube + specimen	0	29.1433	
	3.000	29.0484	−0.0949
Glass tube + specimen + water	0	32.5274	
	3.000	32.4175	−0.1099
Glass tube + copper wire + water	0	12.1619	
	3.000	12.1038	−0.0581

$$\Delta W_{Sb} + \Delta W_s = -0.1099 - (-0.0040) = -0.1059$$
$$\Delta W_{Sb} - \Delta W_s = -0.0949 - (-0.0040) = -0.0909$$

$$2\Delta W_s = -0.0150$$
$$\Delta W_s = -0.0075$$
$$\Delta W_{Sb} = -0.1059 - (-0.0075) = -0.0984$$

$$\Delta W_{H_2O} + \Delta W_s = -0.0581 - (-0.0040) = -0.0541$$
$$\Delta W_{H_2O} = -0.0541 - (-0.0075) = -0.0466$$

Therefore, for explosive antimony,

$$\chi = \frac{-0.72 \times 10^{-6} \times -0.0984}{-0.0466 \times 6.8} = -0.22 \times 10^{-6}.$$

In the foregoing calculation ΔW_w is the apparent change in weight of the water layer between the cylinder of antimony and the wall of the glass tube. Although the values obtained for different specimens did not agree particularly well, the susceptibility of any one specimen could be checked from day to day to well within 0.5%. The magnetic susceptibility of purified benzene was found to be -0.714×10^{-6}, in excellent agreement with the value 0.712×10^{-6} given in the International Critical Tables.

After determining the susceptibility of an explosive specimen, it was crystallized non-explosively by keeping it for 24 hr. at 80° C. and then 24 hr. at 110° C. (4). Its magnetic susceptibility was then redetermined. All measurements on the explosive deposits were made within a few days of their preparation, so that no appreciable crystallization could have occurred (3).

Discussion of Results

The three specimens of explosive antimony used for these measurements are described in Table I.

TABLE I

SPECIMENS OF EXPLOSIVE ANTIMONY USED FOR MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Specimen No.	Wt. Sb., gm.	% $SbCl_3$ in sol'n.	% $SbCl_3$ in metal	Approx. length, cm.	Approx. diam., cm.
1	34 84	15	5	6 5	1
2	13 85	31	6	6	0.3
3	24.53	31	6	6	0.9

Column 4 gives the approximate percentage of antimony trichloride in the metal, as interpolated from the antimony trichloride concentration of the solution (column 3) from which it was deposited (6). Specimens 2 and 3 were very bright and smooth and of uniform diameter. Specimen 1 was bright but was somewhat rough and uncylindrical. The results of the magnetic susceptibility measurements are given in Table II. The results of all determinations are listed.

TABLE II

THE MAGNETIC SUSCEPTIBILITY OF EXPLOSIVE AND OF CRYSTALLINE ANTIMONY

Specimen	$\chi \times 10^6$	Mean $\chi \times 10^6$
No. 1 Explosive	−0.21, −0.21	−0.21
No. 1 Crystallized	−0.42, −0.41	−0.42
No. 2 Explosive	−0.19, −0.19	−0.19
No. 2 Crystallized	−0.44, −0.44	−0.44
No. 3 Explosive	−0.22, −0.22, −0.22	−0.22
No. 3 Crystallized	−0.52, −0.49, −0.[illegible]	−0.50

Mean value of χ for amorphous antimony = -0.21×10^{-6}
Mean value of χ for crystallized antimony = -0.45×10^{-6}

There is a small correction to be made for the diamagnetism of the antimony trichloride ($\chi = -0.36 \times 10^{-6}$) present in these specimens. The assumption that there is 5% of antimony trichloride as such in both the amorphous and crystalline metal changes the values in Table II for the susceptibilities by about $+0.01 \times 10^{-6}$ and -0.01×10^{-6} respectively. These values thus become

χ(explosive Sb) = $-0\ 20 \times 10^{-6}$
χ(crystallized Sb) = $-0\ 46 \times 10^{-6}$
The I.C.T. give χ(crystalline Sb) = $-0\ 87 \times 10^{-6}$.

This discrepancy between the magnetic susceptibility observed for the crystallized specimens and that given in the literature for the polycrystalline metal is probably due to the presence of traces of iron in the electrolytic preparations. The great difficulty in avoiding or correcting for traces of ferromagnetic material in work of this kind is well known (10, p. 505), and it seems fairly certain that iron dissolved in antimony is in a ferromagnetic state (8, p. 373).

As a test of the magnetic purity of the starting material, two polycrystalline rods were cast from the same "chemically pure" antimony that had been used for the anodes in the preparation of the explosive specimens, and their susceptibilities were measured. The value found, *viz*, $-0\ 54 \times 10^{-6}$, is much closer to that of the crystallized specimens than to that given in the literature. It thus seems probable that the presence of iron is the cause of the low diamagnetism of the crystallized material, and that both the amorphous and the crystallized metal are more diamagnetic than the foregoing experiments indicate. If this assumption is correct, the true value for the magnetic susceptibility of amorphous antimony is probably about $-0\ 38 \times 10^{-6}$. The amorphous metal is thus somewhat less diamagnetic than even liquid antimony at the melting point ($\chi = -0\ 49 \times 10^{-6}$). The values are nearly enough alike, however, to suggest that the internal binding is very much the same in the two cases, and that some mechanism other than the disappearance of metallic bonds must account for the loss of metallic properties that occurs when the metal becomes amorphous. The high resistance (at 0° C. about 100,000 times that of ordinary antimony (3)) and its negative temperature coefficient are properties of the material that are difficult to explain unless the disappearance of metallic bonds is assumed.

It has been recently suggested by Prins (9), who has also found explosive antimony to be less diamagnetic than ordinary antimony, that the high resistance of the explosive form is due to the presence of the antimony trichloride, which may exist as insulating films within the metal. In support of this view are the facts that the specific resistance increases with increasing antimony trichloride content, and that the material is distinctly heterogeneous (4). On the other hand, the fact that amorphous films of antimony containing no antimony trichloride show much the same peculiarities with regard to the electrical resistance and its temperature coefficient (7) is definitely opposed to this hypothesis.

Acknowledgment

The writer is indebted to Prof. H. L. Bronson for the loan of the electromagnet.

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A NEW METHOD FOR THE APPLICATION OF LUMINESCENT SCREENS TO GLASS SURFACES[1]

BY W. H. KOHL[2]

Abstract

An outline is given of the various methods for the application of luminescent screens, and their relative merits. Most widespread in use are methods that utilize a liquid binder that enters into a chemical reaction with the glass surface. In other cases, the powder is partially imbedded in the glass surface by a sintering process. The physical characteristics of the luminescent screen are adversely affected by both of these methods. A process based on the activation of the glass surface by a deposit of sulphur is described. The sulphur coating picks up the luminescent powder in a uniform layer when it is brought into contact with the powder. After being removed by means of a moderate heat treatment, it leaves the screen firmly adhering to the glass surface Possible mechanisms for the process are briefly discussed.

History and Current Methods

The coating of glass surfaces with powders, and in particular the coating of the inside wall of a glass envelope, constitutes an important process in the manufacture of cathode ray tubes. In the early Braun tube (4) the luminescent screen was painted on a mica disc, which was held in position close to the inside of the face of the bulb. Viewed from the outside, the luminescent spot was necessarily of low intensity, owing to the absorption of light in the mica disc and in the glass wall. Varley (15), who worked with Braun in Strassbourg, therefore replaced the mica disc by a glass disc, and finally applied the screen directly to the inside wall of the tube.

In order to make the screen adhere to the glass surface, the powder was either mixed with sodium silicate (water glass) and painted on with a brush, or dusted on to a film of water glass and then sintered on to the glass by heat treatment. Screens made in this fashion are liable to show brush marks and are easily discolored or burnt when exposed to the electron beam. This is due to a reduction of the binder and its chemical reaction with the glass. Potassium water glass has lately been used to greater advantage as a binder in this method (1, pp. 85-88). L. M. Hull (8) used a lacquer binder instead of water glass.

Another method in wide use up to the present day is that developed by Everett and described by Sir J. J. Thomson (14). The powder is allowed to settle slowly from a suspension in alcohol. "When the deposit has reached the requisite thickness, the rest of the suspension is drawn off and the deposit allowed to dry; when dry it sticks quite firmly to the plate." Unless sintered into the glass, however, such screens are very sensitive to mechanical shocks, and therefore not suitable for shipment.

It is from another viewpoint that carbon compounds such as alcohol, acetone, ethyl oxalate, glycerine, and others, are not suitable as binders for screen materials. It has been observed throughout the development of the Braun tube that such screens are liable to build up surface layers, which are apt to block the electron stream and prevent it from hitting the fluorescent material proper (1, 15). The phenomenon observed is the emanation, from the centre of a dark circular area around the point of impact of the beam as centre, of fluorescent streamers that travel towards the edge of the screen where the electrons, which glide over the charged surface, are able to excite the outer regions to fluorescence. Stewart (11) has given an account of the formation of insulating films caused by electron and ion bombardment in the presence of the slightest traces of organic vapors in an evacuated tube ($p = 10^{-6}$ mm. of mercury) for electron velocities in the range 190 to 210 volts. Stewart points out that these films are formed only at the point of impact of the rays on the surface, and may be attributed to carbon compounds formed by the polymerization of organic vapors. They are formed on glass and metal surfaces that are exposed to bombardment by the particles in question.

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Black circular areas on the lower side of an anode disc with the aperture as centre and interference fringes at the edge were repeatedly observed by the author during the earlier stages of the development of cathode ray tubes. In each of these cases the screen was put on with an organic binder.

The exclusion of such binders is essential for the reasons given above. The only alternative method left for the application of luminescent screens seems to be that of Espe (6; 1, p. 86). The glass surface is wetted with distilled water and the fine powder dusted onto it so as to form a uniform layer. The blank is then heated to a temperature near the softening point of the glass, so that the powder particles sink into the glass and are firmly imbedded in it after the glass has cooled down. Particles not in firm contact with the glass may then be removed with a brush. Such screens have the appearance of frosted glass and withstand the bombardment by a high energy beam better than others, owing to the high heat conductivity of the imbedded screen particles. This may be further increased by admixing with the powder a glass dust of a low melting point. Plots of the luminous intensity of the fluorescent spot as a function of the energy input are given by Ardenne (1, pp. 85-88) for a screen of $CaWO_4$ prepared with a potassium silicate binder in one case, and without any binder, but sintered only, in the other. The plots disclose a superior and almost linear characteristic for the sintered screen.

Unfortunately, the luminous intensity of the spot on the screen is partly dissipated in the glass wall and forms a "halo" or "spurious rings" around the spot proper. Hughes (7) and v. Ardenne (2, 3) have studied the causes of the formation of this halo, and the latter suggested means for its reduction. Assuming a perfectly concentrated electron beam exciting fluorescence in one particle of the screen surface, it is found that the halo is due to total reflection of the fluorescent radiation at the glass-air interface of the glass wall. The radius of the halo will be approximately twice the thickness of the wall. Furthermore, it will be larger for a screen particle that is partly imbedded in the glass wall by the sintering process than for a particle that is but loosely bound to the surface by a binder and has a smaller contact area with the glass. Photometric measurements of the relative intensity of the halo with respect to the total brightness of the luminescent radiation disclose that 25 to 28% of the total luminescent radiation is dissipated in the halo in a sintered screen and only 1½ to 4% in a loosely bound screen. The reduction of the diameter and the intensity of the halo is of great importance for the perfection of television images, as well as for obtaining sharp oscillographic curves. It requires the development of special binders of low absorption coefficients and special chemical characteristics. Many workers in the field strive towards this end, and the results obtained are generally guarded with great care. A method that would combine the advantage of a loosely bound screen with the absence of a physical binder, seems to be an ideal solution of the problem.

During a number of years spent on the development of cathode ray tubes, the author encountered in the preparation of fluorescent screens all the difficulties that are described above in part. Suspensions of the powder in acetone and in amyl acetate, which were sprayed on to the glass wall, gave smooth screen surfaces that responded well to the electron beam for a short time, but showed marked deterioration of brilliancy and charge effects, even in gas filled tubes, after a day or so. It was at this stage that a fundamentally different method, one that did not involve the use of organic binders, was sought.

Description of New Method

H. W. Parker* observed that a condensate (obtained by burning sulphur in air) on the glass wall easily picked up the powder in a thin and uniform layer when the powder was put into the bulb, and the bulb revolved over a sharp flame. A uniform sintered screen that could not easily be removed from the glass was thus formed.

A further investigation of the possibilities of sulphur as a binder was suggested to the author and led to the following process, which was developed during the summer of 1933, and has been in use in this laboratory ever since, with only slight modifications.

Experimental tests of electrode structures, cathode designs and luminescent materials are for economic reasons generally carried out with small tubes. Radio tube blanks are useful for this purpose. The application of screens to the face of such envelopes will be described first.

Coating of Small Blanks

A small glass container (10 cc.) is filled with carbon disulphide† and heated electrically so that the liquid boils quietly (b.p. 46° C.). When lit with a match, the vapor burns with a light blue flame about two inches long. The

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**Chief Engineer of Rogers Radio Tubes Limited.*

†*Carbon disulphide is a volatile liquid and poisonous. Its vapor pressure at 1 atm. is 300 mm. of mercury. The vapor forms an explosive mixture with air. It should, therefore, be handled with care.*

blank to be coated is carefully cleaned and held over the flame so as to partially cover it. The products of the chemical reaction are carbon dioxide, sulphur dioxide, sulphur trioxide, and sulphur due to incomplete combustion. Sulphur trioxide is formed to a small extent in the presence of water vapor. For the purpose of the present description of the technical features of the process, it will be assumed that sulphur vapor is the main product of the reaction. A few seconds after the blank is exposed to the vapor stream, a deposit forms suddenly on the glass wall and gradually becomes heavier. The blank is filled with a dense cloud. When the deposit is of a yellowish green color, the blank is removed from the flame and allowed to cool. The deposit is then wiped from the wall of the blank with a cloth, except for the part that is to carry the screen. The fluorescent powder, which must be in a free flowing state, *i.e.*, dry and of uniformly small particle size, is put into the blank and brought into contact with the sulphur coating by shaking it quickly with a circular motion. The sulphur coating picks up a uniform thickness of powder that is determined by the thickness of the original coating. The excess powder is removed by turning the blank upside down and shaking it violently. The wall is then wiped clean with a cloth and the edge of the screen reduced to the desired diameter. The sulphur deposit on the screen is driven off by holding the blank over a Bunsen flame of moderate temperature for a few minutes. This completes the process. A perfectly uniform screen adheres to the surface of the glass. The screen cannot be shaken off after exhaustion of the tube, but it can easily be removed with a cloth if another screen is to be put on. Blanks of medium size (3 in. screen diameter) can be coated in the same way. While exposing the blank to the vapor it is advisable to rotate it slowly in a holder, to ensure a uniform deposit of the vapor on the screen surface. The coating of such small blanks is carried out very easily in a very short time and at a minimum cost. The excess powder from the coating of one blank can immediately be used for the next one.

Coating of Large Blanks

Large-sized blanks for cathode ray tubes of 5 in. or greater screen diameter require a specially designed double wall chimney that guides the vapor towards the screen surface, and prevents its condensation on the neck of the tube. This funnel ends in a specially designed mouthpiece which has a hollow glass cone with its apex pointing downwards, and which is supported in the inner tube. It serves to distribute the rising stream of vapor over a spherical angle and prevents it from hitting the centre of the screen surface directly. The blank is rotated slowly during this stage of the process; after about 10 min. a heavy deposit of sulphur is obtained. It was found useful, though not necessary, to cool the surface by means of water in a cylindrical container that fitted tightly over the face of the blank and rotated with it. After it has circulated within the bulb, the vapor is pumped off through the funnel by means of a water jet pump. This protects the operator from escaping sulphur vapors. The blank is then cleaned with a cloth, with which the sulphur deposit may be easily removed from the wall. In order to obtain a uniform screen, the powder should be whirled into a cloud before it makes contact with the surface. If the powder makes its first contact with the screen in a mass, streaks are liable to be left, but after the original contact the powder is allowed to slide over the surface in bulk.

Physical Qualities of the Screen

The screen material is generally passed through a 200 mesh sieve to ensure approximately uniform particle size. The diameter of a particle was, therefore, on the average, of the order of 50 μ. Whether there exists an optimum particle size, as found by A. v. Buzágh (5) for microscopic particles in a liquid suspension adhering on surfaces which consist of the same material as the particles, has not been determined. When observed under a microscope, the completed screen appears as a fairly close packing of one layer of particles with interspaces on boundary lines unoccupied, owing to the irregular shape of individual particles. Here and there a larger particle rests on top of this layer. The screen has a transmittance approximately that of frosted glass, and appears white, gray, or whitish yellow, depending on the natural color of the screen material. Electrons penetrate only to about 10^{-4} cm. into the dielectric, as determined by the equation $d = KV^4$, where d is the depth of penetration, V is the volt equivalent of electron beam velocity, and K is a constant. For potentials commonly applied to cathode ray tubes, the depth of penetration is very small. A thin uniform screen is therefore most efficient.

Screens prepared in the manner described above are of high brilliancy, and show no deterioration other than that due to the quality of the screen material itself. They are equally suitable for gas filled and high vacuum type tubes. Their mechanical strength is not affected by the heat treatment of the tube necessary in the exhaustion process, during which the temperature is raised to 480° C. The tenacity with which the surface forces hold the powder is evident from the following simple tests. The screen cannot be separated from the glass by a strong stream of air, by any violent shocks, or by filling the tube with water and then drying it again over a flame. However, the coating can easily be wiped off with a cloth. This shows that the particles are loosely bound to the surface. Finished screens can be left exposed to the atmosphere for any length of time before being sealed and exhausted. Sulphur coated blanks may also be stored for days before the powder is applied. It is advisable, however, to complete the process without interruption.

Consideration of the Mechanism of the Process

No attempt will be made in this preliminary report to present a theory of the mechanism of this process. Lack of time and equipment has made quantitative measurements impossible so far. A closer study has recently been undertaken at the McLennan Institute of the University of Toronto.

A few observations will be reported, however, and possible correlations with other phenomena in the field of surface physics pointed out as a suggestion for further research.

A thin glass disc was moved slowly through a carbon disulphide flame and then observed under a microscope. A matrix of closely arranged tiny droplets covering the surface was thus formed. The disc was then moved through the flame again, observed, and this procedure repeated several times. On repeated exposures to the flame, the size of the globules gradually increased and the matrix became less dense, until finally several adjacent globules combined to form elongated, irregularly shaped bands, which were interlaced and looked like the pattern of a labyrinth. The formation of such droplets by the condensation of vapors on metal or glass surfaces is a well known phenomenon, and was recently studied carefully by Tammann and Boehme (13). They investigated the condensation of water vapor on metal and glass surfaces, and, with a microscope, counted the number of droplets per unit area. It was found that condensation centres exist on the surface, and that, after a deposit is removed with the aid of heat, repeated condensations lead to the formation of individual droplets at the same points on the surface. The number of droplets formed per unit area on different metals shows a correlation with their position in the Volta series. Condensation occurs most readily at crystal interfaces and where there are tool marks. The number of droplets formed on glass was only half that on gold (200 per 0 01 mm.^{2} on gold).

The activation of the glass surface by the sulphur deposit may be explained in one of the following ways:

1. The sulphur may act as a cleaning agent and allow the powder particle to come in contact with a clean surface after the evaporation of the droplet underneath, and be held by surface forces.

2. A very thin layer of amorphous sulphur might adhere to the surface even after the heat treatment, and act as a binder. This is considered to be unlikely, as the slightest traces of sulphur would tend to poison the cathode, and this would affect the thermionic emission. No such effect was ever observed.

3. The powder particles are undoubtedly charged electrically, owing to their mutual friction during the process of application. On the other hand, the glass surface is most probably charged during the exposure to the sulphur vapor, in a manner similar to that described by Stimson (12) for the building up of charges on hot metallic surfaces during the adsorption of gases. The role of the sulphur may then be to charge the glass surface and thus cause the binding of the powder by electrical forces.

To clarify this mechanism and ascertain whether other vapors would have a similar effect should prove to be an interesting study.

Acknowledgment

The author wishes to express his indebtedness to Mr. H. W. Parker for his original suggestion and continued interest during the development of this process. Mr. E. S. Rogers has kindly authorized the publication of this article.

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THE SORPTION OF WATER VAPOR ON CELLULOSIC MATERIALS[1]

BY EDGAR FILBY[2] AND O. MAASS[3]

Abstract

A direct method used for measuring the adsorption of water vapor on cellulosic materials and in which a number of improvements have been made is described. It is ensured that no vapors other than water are present no matter how long a time is required for the establishment of equilibrium. The adsorption and desorption isotherms of standard cellulose, spruce wood, surgical cotton, Kodak rag cellulose and bleached sulphite have been measured, and the data which indicate the time required for the establishment of true equilibrium have been given. The data of Urquhart and Williams (6, 7) for standard cellulose determined by an indirect method in 1926 have been shown to be correct.

Introduction

This paper deals with the further development of a method used by one of us for measuring the sorption of vapors such as water and alcohol on adsorbing materials such as cellulose and wood.

A McBain-Bakr spring balance of quartz fibre, sensitive to about 1 part in 20,000 of the total weight suspended, is used to measure the sorption, which, at saturation, amounts to 20 or 30% of the dry weight.

The sample to be investigated is suspended on the spring balance in a glass tube and subjected to a constant vapor pressure by connecting the tube to a bulb containing the liquid sorbate. In this way the relative vapor pressure of the sample and that of the liquid used as the source of vapors may be regulated by thermostatically controlling each separately.

The system contained neither stopcocks nor mercury seals, since both are subject to criticism, the stopcocks developing leaks and the mercury being adsorbed appreciably on cellulose at high-vacuum pressures.

The curves as established are of the same "S"-form as that indicated by previous workers (1, 2, 4, 5, 6, 7); however the time required for equilibrium to be established is in some cases found to be considerably longer owing to the somewhat different technique employed.

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[1] *Manuscript received June 11, 1935.*
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Experimental

Apparatus

As previously stated the McBain-Bakr (3) spring balance was made from a fine quartz fibre. These fibres were made by pulling out quartz rod after it had been heated in an oxy-acetylene flame, and were wound into spirals of half-inch diameter and about 50 turns to the inch by passing them through a small gas jet on to a revolving steel rod.

Each cell was constructed of glass tubing of about 2½ ft. in length and one inch diameter. This was sealed off at both ends, with a hook at one end to which the balance and suspended sample could be attached. At a short distance from the hook end there was inserted a side tube that could be connected to the water bulb.

The two thermostats, one for the cells, the other for the water bulb, were fitted with cooling coils, heating lamps and thermoregulators, which were sensitive to 0 01° change in temperature. A diagram of the vacuum system is shown in Fig. 1 in which one cell and spring balance is drawn in full and the position of the other four indicated.

Manipulation

After the balances were made and fitted with central rods (W. B. Campbell (1)) as shown in Fig. 1, they were tested for Hook's law by measuring the length from the end of the central rod to the bottom of the spiral, shown in Fig. 2, with varying loads. The balance and sample were then suspended in the cell and the end sealed off, a process that required considerable technique.

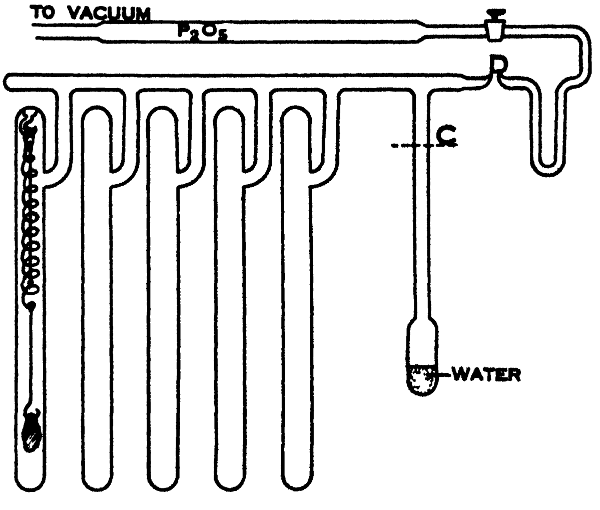

FIG. 1. *Sorption measuring system.*

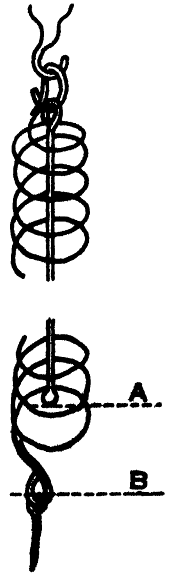

FIG. 2. *Quartz spiral.*

When five cells, each containing a spring balance and suspended sample were fitted as shown in Fig. 1, the system was sealed at *C*, and evacuated through the phosphorus pentoxide tube which was surrounded by liquid air to prevent contamination from the mercury vapor pumps at high-vacuum pressures. The entire system was flushed out several times with dry helium, then the pump left on for a few days until a pressure of less then 0.0001 mm. of mercury was registered in a McLeod gauge attached between the "U" tube and the pump. This low pressure was found to remain constant for 12 hr. after the pumps had been cut off.

During this process, measurements of the length shown between *A* and *B* Fig. 2, were read until the value was constant. The system was then filled with dry helium and the water bulb attached at *C*. The water in the bulb was freed from air by repeatedly freezing, cooling and evacuating it until such a procedure caused no change in pressure in the McLeod gauge. The system was again flushed out with helium, the water bulb was immersed in liquid air, and the process of evacuation allowed to continue until the pressure could not be read on the McLeod gauge. The system was then sealed off from the pumps and phosphorus pentoxide tube at *D*, leaving a closed evacuated system containing the sorption balance and solid and liquid phases to be studied.

The remainder of the experimental procedure consisted in measuring the length of the spiral balances under varying conditions of relative vapor pressures. This was done by keeping the cells at 20.0° C. and varying the temperature of the water bulb. First, the bulb was set at liquid air temperatures and left until equilibrium was established, readings on the spirals being taken every few hours. This was repeated at different temperatures each higher than the preceding one until finally the water bulb was thermostatically controlled at about 19° C., which gave a relative vapor pressure of about 94%. Water was then distilled from the bulb into the cells in order to saturate the samples. When this was accomplished the temperature of the water bulb was lowered and the vapor distilled off from the samples. Desorption equilibrium values were then obtained at various intervals until at liquid air temperatures the phosphorus pentoxide dry weight was again reached. In this manner the adsorption isotherm for the materials investigated were established. A calibrated Becker cathetometer was used to measure the length of the spirals.

Materials

A sample of white spruce wood 1 mm. thick was taken from the centre of a log. Cutting across the grain and limiting the thickness to 1 mm. was found to speed up diffusion of the vapor into the sample. The spruce wood was suspended on spiral balance No. 1.

Spiral balance No. 2 carried a piece of purified cotton obtained from bleached surgical cotton by seven 12-hr. extractions with 1% boiling sodium hydroxide, after which the cotton was washed free from base with distilled water. The process was completed by acidifying the cotton with 1% acetic acid and washing it free from acid.

The sample of standard cellulose on spiral balance No. 3 was prepared as follows. A 75 gm. batch of raw cotton that had been hand picked free from seeds and foreign matter was extracted with ethyl alcohol for four periods of four hours each. Four two-hour extractions were then carried out with diethyl ether, after which the cotton was subjected to a continuous ten hour extraction with 1% boiling sodium hydroxide, during which a total volume of 10 litres was used. The cotton was then washed with four litres of boiling water, and cold water, five to six litres, was added to cool the batch, which was then washed on a Buchner funnel with five litres of water and dried by means of a suction pump. The product was next soaked in 1% acetic acid for about two hours, washed free from acid with 10 litres of water and allowed to dry *in vacuo* at about 40° C. All solutions were made with distilled water, and all water used was previously boiled to expel dissolved oxygen.

Spiral balance No. 4 carried a sample of Kodak rag cellulose, and spiral balance No. 5, a sample of bleached sulphite pulp that had been allowed to stand in distilled water for a period of 12 hr.

Results

The spirals were carefully calibrated with known weights and tested for the relation $S = \frac{E}{W}$, where S is the sensitivity and E is the elongation caused by a weight of W grams. In the following tables are shown (i) the sorption values found when the samples were subjected to definite vapor pressures, and (ii) the desorption values of the same samples. In Table I the data recorded for standard cellulose are given in detail to indicate the time required for equilibrium to be established. Column 1 shows the time in hours, *i.e.* the time from the adjustment of the temperature of the water bulb to T_2° C. to the time of reading the length AB. T_1 is the temperature of the sample and T_2 that of the thermostat surrounding the water bulb. Where no temperature is recorded under T_2 it means that the sample was subjected to evacuation prior to the sealing off of the apparatus. L, in millimetres, is the distance between the points A and B, from which the elongation can be calculated. The first value at each temperature, T_2, given is that at which equilibrium was expected, and the subsequent values are recorded to indicate further change if any. It will be seen that in the sorption at low vapor pressures, equilibrium is established fairly rapidly, but at higher pressures and for desorption long intervals of time are required. It is of interest to note that after desorption the liquid air value was the same within experimental error. The last two columns show the percentage of water and the percentage relative vapor pressure taken as the final value. The percentage of water sorbed by the sample was calculated in terms of the dry weight. The relative vapor pressure was calculated from data obtained from the International Critical Tables.

TABLE I

SORPTION OF WATER VAPOR ON STANDARD CELLULOSE AND DESORPTION OF WATER FROM STANDARD CELLULOSE SATURATED WITH WATER VAPOR

Time, hr.	T_1, °C.	T_2, °C	L, mm.	E, mm.	% Water on sample	% R.v.p. in system
Sorption						
12	20.0		1.94			
36	20.0		1.90			
60	20.0		1.90			
84	20.0		1.94			
10	20.0	Liquid air	1.95			
20	20.0		1.94			
17	20.0	Solid CO_2 and ether	1.96			
26	20.0		1.94			
40	20.0		1.94			
1	20.0	−20	2.71			
3	20.0	−20	2.73	0.83	0.80	4.24
2	20.0	−6.5	4.89			
4	20.0	−6.5	4.87	2.98	2.85	15.11
24	20.0	0.0	5.77			
28	20.0	0.0	5.79			
36	20.0	0.0	5.79	3.89	3.73	26.12
32	20.0	11.5	8.85			
39	20.0	11.5	8.85			
46	20.0	11.5	8.86	6.96	6.66	58.04
13	20.0	12.0	9.21			
26	20.0	12.0	9.20			
31	20.0	12.0	9.20	7.30	6.98	59.98
20	20.0	14.0	10.27			
66	20.0	14.0	10.28			
78	20.0	14.0	10.27			
86	20.0	14.0	10.27	8.37	8.01	68.36
17	20.0	16.0	11.88			
54	20.0	16.0	11.84			
62	20.0	16.0	11.87			
86	20.0	16.0	11.88	9.98	9.56	77.75
23	20.0	19.0	17.69			
40	20.0	19.0	17.78			
80	20.0	19.0	17.77			
95	20.0	19.0	17.85	15.9	15.3	93.9
21	20.0	19.5	21.73			
42	20.0	19.5	21.79			
50	20.0	19.5	22.03			
65	20.0	19.5	21.60	20.	19.	96.9
10	20.0	20.1	100*			
58	20.0	20.1	54.0			
82	20.0	20.1	54.2			
94	20.0	20.1	55.0	53	51	100

**The high saturation value found at the end of 10 hours was due to water condensing on the sides of the cell and being absorbed on the sample by actual contact.*

TABLE I—*Concluded*

SORPTION OF WATER VAPOR ON STANDARD CELLULOSE AND DESORPTION OF WATER FROM STANDARD CELLULOSE SATURATED WITH WATER VAPOR

Time, hr.	T_1, °C.	T_2, °C	L, mm.	E, mm.	% Water on sample	% R.v.p. in system
Desorption						
82	20.0	19.0	20.99			
115	20.0	19.0	21.06			
176	20.0	19.0	20.50			
194	20.0	19.0	20.45			
224	20.0	19.0	20.46	18.5	17.5	93.9
24	20.0	18.0	17.56			
94	20.0	18.0	17.34			
138	20.0	18.0	17.24			
160	20.0	18.0	17.25	15.3	14.5	88.3
24	20.0	16.0	14.37			
90	20.0	16.0	14.15			
128	20.0	16.0	14.09			
138	20.0	16.0	14.08	12.18	11.55	77.75
45	20.0	12.0	10.74			
60	20.0	12.0	10.69			
94	20.0	12.0	10.67			
108	20.0	12.0	10.67	8.77	8.30	59.98
12	20.0	8.0	9.10			
36	20.0	8.0	9.00			
60	20.0	8.0	9.00			
108	20.0	8.0	9.00	7.10	6.73	45.88
31	20.0	2.0	7.50			
48	20.0	2.0	7.45			
76	20.0	2.0	7.25			
110	20.0	2.0	7.25	5.35	5.07	30.2
6	20.0	−11.0	4.82			
24	20.0	−11.0	4.51			
48	20.0	−11.0	4.52			
60	20.0	−11.0	4.51	2.61	2.47	10.18
24	20.0	Solid CO_2 and ether	1.99			
48	20.0		1.95			
72	20.0		1.94			
96	20.0		1.95			
12	20.0	Liquid air	1.93			
25	20.0		1.90			
72	20.0		1.92			
95	20.0		1.91			

In Table II are recorded the final sorption and desorption values for the other samples.

In every case it was found that the weight *in vacuo* corresponded with the weight when the temperature was that of liquid air to within the accuracy with which measurements could be made.

TABLE II

SORPTION AND DESORPTION VALUES FOR VARIOUS CELLULOSIC MATERIALS

T_1, °C.	T_2, °C.	% Water in sample	% R.v.p. in system	T_1, °C.	T_2, °C.	% Water in system	% R.v.p. in system
Sorption				Desorption			
White spruce							
20.0	Liquid air			20.0	19.0	28.2	93.9
20.0	Solid CO_2 and ether			20.0	18.0	24.1	88.3
20.0	−20	1.84	4.24	20.0	16.0	19.01	77.75
20.0	−6.5	4.60	15.11	20.0	12.0	14.13	59.98
20.0	0.0	6.23	26.12	20.0	8.0	11.37	45.88
20.0	11.5	11.53	58.04	20.0	2.0	8.41	30.20
20.0	12.0	11.96	59.98	20.0	−11.0	4.21	10.18
20.0	14.0	13.67	68.36	20.0	Solid CO_2 and ether		
20.0	16.0	16.40	77.75	20.0	Liquid air		
20.0	19.0	25.2	93.9				
20.0	19.5	30	96.9				
20.0	20.1	35	100				
Bleached surgical cotton							
20.0	Liquid air			20.0	19.0	17.5	93.9
20.0	Solid CO_2 and ether			20.0	18.0	14.3	88.3
				20.0	16.0	11.95	77.75
20.0	−20.0	0.99	4.24	20.0	12.0	7.92	59.98
20.0	−6.5	2.82	15.11	20.0	8.0	6.23	45.88
20.0	0.0	3.64	26.12	20.0	2.0	4.64	30.20
20.0	11.5	6.44	38.04	20.0	−11.0	2.52	10.18
20.0	12.0	6.74	29.88	20.0	Solid CO_2 and ether		
20.0	14.0	7.74	68.36				
20.0	16.0	9.24	77.75	20.0	Liquid air		
20.0	19.0	15.2	93.9				
20.0	19.5	19	96.9				
20.0	20.1	32	100				
Kodak rag cellulose							
20.0	Liquid air			20.0	19.0	17.8	93.9
20.0	Solid CO_2 and ether			20.0	18.0	14.5	88.3
				20.0	16.0	11.23	77.75
20.0	−20	0.94	4.24	20.0	12.0	7.97	59.98
20.0	−6.5	2.60	15.11	20.0	8.0	6.26	45.88
20.0	0.0	3.46	26.12	20.0	2.0	4.64	30.20
20.0	11.5	6.49	58.04	20.0	−11.0	2.40	10.18
20.0	12.0	6.77	59.98	20.0	Solid CO_2 and ether		
20.0	14.0	7.84	68.36				
20.0	16.0	9.34	77.75	20.0	Liquid air		
20.0	19.0	15.4	93.9				
20.0	19.5	20	96.9				
20.0	20.1	39	100				

TABLE II—*Concluded*

SORPTION AND DESORPTION VALUES FOR VARIOUS CELLULOSIC MATERIALS

T_1, °C.	T_2, °C.	% Water in sample	% R.v.p. in system	T_1, °C.	T_2, °C.	% Water in system	% R.v.p. in system
Sorption				Desorption			
Bleached sulphite pulp							
20 0	Liquid air			20 0	19 0	21 3	93 9
20 0	Solid CO_2			20 0	18 0	17 4	88 3
	and ether			20 0	16 0	13 30	77 75
20 0	−20	1 33	4 24	20 0	12 0	9 46	59 98
20 0	− 6 5	3 40	15 11	20 0	8 0	7 44	45 88
20 0	0 0	4 63	26 12	20 0	2 0	5 63	30 2
20 0	11 5	8 08	58 04	20 0	−11 0	3 94	10 18
20 0	12 0	8 48	59 98	20 0	Solid CO_2		
20 0	14 0	9 67	68 36		and ether		
20 0	16 0	11 45	77 75	20 0	Liquid air		
20 0	19 0	19	93 9				
20 0	19 5	23	96 9				
20 0	20 1	33	100				

TABLE III

COMPARISON OF DATA OF AUTHORS WITH THAT OF URQUHART AND WILLIAMS

Relative humidity, %	Water in sample, %			
	Standard cellulose (F and M)	Bleached surgical cotton (F and M)	Kodak rag cellulose (F and M)	Scoured cotton (U and W)*
Sorption				
4 24	0 80	0 99	0 94	1 4
15 11	2 85	2 82	2 60	2 6
26 12	3 73	3 64	3 46	3 5
58 04	6 66	6 44	6 49	6 3
59 98	6 98	6 74	6 77	6 5
68 36	8 01	7 74	7 84	7 5
77 75	9 56	9 24	9 34	9 1
93 9	15 3	15 2	15 4	14 9
96 9	19 0	19 0	20 0	17 6
Desorption				
93 9	17 5	17 5	17 8	81 1
88 3	14 5	14 3	14 5	14 8
77 75	11 55	11 05	11 23	11 3
59 98	8 30	7 92	7 97	8 2
45 88	6 73	6 23	6 26	6 4
30 2	5 07	4 64	4 64	4 6
10 18	2 47	2 52	2 40	2 5

Data received in private communication from A. R. Urquhart.

Discussion

A method for the determination of the sorption of water vapor on cellulosic materials has been described. The new features are greater sensitivity of spiral, elimination of all vapors including mercury and air, complete isolation of materials examined from contact with anything but water vapor over an indefinite period. To amplify the last statement it may be said that it is of advantage to subject the cellulosic materials to repeated hysteresis cycles in such a manner that the interference of such factors as contact with air, etc. is impossible. Finally when various cellulosic materials are to be compared the necessity of absolute identity of conditions for purposes of comparison is obvious.

The results obtained with cotton are found to be in agreement with those of Urquhart and Williams (Table III). In a paper by Maass and Pidgeon (4) the following statement was made regarding sorption measurements on wood and cotton:—

"Little of the work which has been done is entirely free from objection. In even the most careful determinations of the adsorption by cotton cellulose the amount of adsorption was measured indirectly." This statement is certainly erroneous in so far as the work of Urquhart and Williams is concerned. Their results are as nearly correct as it is possible to obtain them. On the contrary, the values obtained by Maass and Pidgeon at high relative humidities have been shown to be much too low, owing to inexperience regarding the time required for equilibrium to be established under these conditions. The main object of the paper of Maass and Pidgeon, to show the similarity in type of curve (sorption and desorption) between wood and cellulose and also to show the markedly greater adsorption by wood, has been amply confirmed both by Grace and Maass and the work described in this paper.

It may not be out of place to set forth the reasons why the direct method was considered to be the one giving more accurate values. It is probably true that in the indirect method the pressure is very rapidly equalized throughout a 100 cc. volume—so rapidly that sorption proceeds at uniform rate throughout the sample. This can be true, however, only in the entire absence of air or similar gas. Even a very small quantity of air will be driven by flow of water vapor into any pockets where sorption is taking place, and here sorption will be delayed by diffusion of vapor in one direction against diffusion of air in the opposite direction. In any case the main point is not whether sorption should take place at a constant vapor pressure, a phenomenon that is of course impossible, because it is necessary to cause a change in vapor pressure in order to cause sorption. The real point is whether the sample reaches its equilibrium by continual sorption *in one direction*, as compared with a part of the sample (whether that part be a part—the outside—of a single fibre or all the fibres) in one portion of the apparatus over-reaching the equilibrium value and then establishing equilibrium from the opposite direction. From the statement made by Urquhart and Williams (7) it is evident that the vapor pressure is temporarily higher than the final value. Even assuming that the vapor pressure is equal throughout the space, this can mean only that outside layers of cellulose approach equilibrium with this high vapor pressure and later lose moisture, which is adsorbed by the inside layers. Hence the two portions reach the value from opposite directions. It is evident however that sorption is very rapid, since the cotton reduced the vapor pressure to 2 mm. although that of the water supply was 23.7 mm., but cooling, etc., delayed evaporation. Again, the tap was closed when the pressure was 11 mm. (63%), and the pressure sank to 8 mm. (46%). Some portion of the cotton must have almost reached equilibrium with the 63% relative vapor pressure, and later lost water to such an extent that equilibrium with 46% relative vapor pressure was established. The extent of this error depends on the size of the step taken and the portion of the curve concerned. If steps are small the error is small and this was undoubtedly the case in Urquhart and Williams' work.

Finally in regard to the foregoing it is left to the reader to judge the relative merits of the direct and indirect methods for measuring sorption on cellulosic materials. However, the data at high relative vapor pressures obtained by Maass and Pidgeon with cotton* are considerably too low, because time was not allowed for true equilibrium to be established, and their statement regarding the demerits of the indirect method is regretted. The errors, if any, supposed to be inherent in the indirect method, evidently had a negligible effect on the results of Urquhart and Williams.

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**Purification of the cotton sample used by Pidgeon and Maass was not as extensive as in the case of the samples examined in this investigation. Continued treatment with alkali (even 1%) increases the sorptive power of the cotton until a limiting value is reached. The isotherm obtained by Pidgeon and Maass is affine to that of Urquhart and Williams up to a relative humidity of 70%, the values being 17% lower in the former case. At relative humidities greater than 70% the values are too low as stated above, but differences due to the fact that equilibrium had not been established are not as large as would otherwise appear.*

THE HYDROGENATION OF ALBERTA COALS

II. COMPARATIVE DATA ON THIRTEEN COALS OF VARIOUS RANKS AND TWO SUSPENSION MEDIA, TETRALIN AND LIQUID PETROLATUM[1]

By E. H. Boomer[2], A. W. Saddington[3], and J. Edwards[4]

Abstract

Thirteen Alberta coals of graded rank have been hydrogenated in the presence of tetralin at 450° C. and in the presence of liquid petrolatum at 425° C. Tetralin is superior to liquid petrolatum owing, it is believed, to its efficiency as a hydrogen carrier and its solvent action on coal. The use of tetralin or materials of similar chemical constitution in a commercial process is considered possible, and the greater cost of the medium might be more than offset by its greater efficiency as compared with the ordinary heavy oils.

A definite progression from old to young coals has been shown by increasing yields of volatile oil, gas and water, and decreasing yields of pitch and coke.

Conversions of coal to oils, water and gas as high as 96 7% with tetralin and 81 6% with liquid petrolatum on the dry, ash-free basis have been reported.

Introduction

In the first paper of this series (4) the results of a preliminary investigation on the hydrogenation of three Alberta coals in various media were reported. This work gave evidence enabling a choice of favorable conditions for a more comprehensive investigation of Alberta coals.

The present paper deals with the hydrogenation of 13 coals of graded rank, including all classifications from semi-anthracite to lignite, by two standard methods. One series was carried out at 450° C. with tetralin (1,2,3,4-tetrahydronaphthalene) as suspension medium, and the other with liquid petrolatum as medium at 425° C. Molybdic oxide was employed as catalyst in both series.

The results have confirmed the advantages of a medium such as tetralin, and thrown some further light on the mechanism of the reactions. They have shown that a hydrocarbon oil, typified by liquid petrolatum, can serve also, though less efficiently, as a suspension medium. Finally, the results demonstrate the suitability of several Alberta coals for use in the hydrogenation process in showing that lignitic coals, and to a lesser extent bituminous and sub-bituminous coals, can be converted nearly completely into liquid and gaseous products. The result would be important in the event that economic conditions warranted the use of the process as a source of oils. The primary economic requirements, both of which are fulfilled in Alberta, are sources of suitable cheap coal and hydrogen.

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Materials and Apparatus

The series of 13 coals studied were obtained through the courtesy of Prof. E. Stansfield of the Research Council of Alberta. They were taken as samples in the ordinary course of the 1930 Alberta Coal Survey. A complete description and analysis of these coals is given in Tables I and II and in Fig. 1. The authors wish to acknowledge gratefully the assistance and advice in regard to the analytical data so generously provided by Professor Stansfield and Mr. W. A. Lang of the same laboratory.

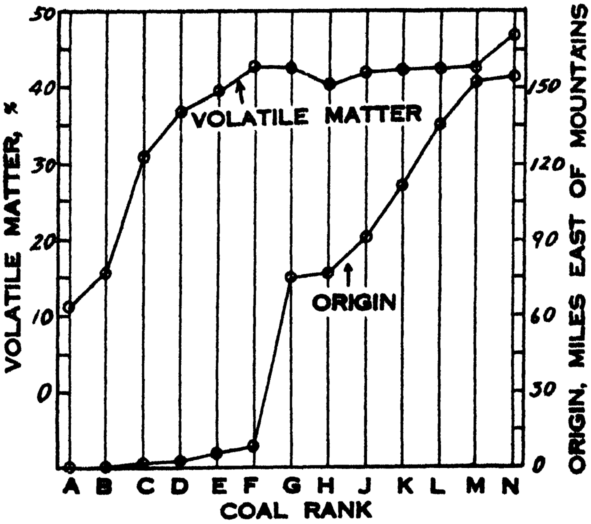

FIG. 1. *Proximate analysis of dry, ash-free coal, and geographic origin of coals, in miles east of Rocky Mountains face.*

The coals have been arranged in order of maturity, and have been assigned letters in order of the sequence, in addition to their sample number. The sequence starts with A, a semi-anthracite coal and ends with N, a lignite coal. The coals showed definite trends in three general properties through the sequence. First, there was an increase in moisture content; second and third, there was a decrease in calorific value and in carbon-hydrogen ratio, with decreasing maturity. Fig. 1 shows the proximate analysis of the coals in graphical form and the position of origin of each sample with respect to the eastern face of the Rocky Mountains. Samples A and B were taken on the mountain face, C and D in the foothills immediately east, E and F about 60 miles east of the mountain face; a more or less regular increase in distance from the mountain face will be noticed to N, a point 160 miles east. There is an obvious parallel between the rank of the coals and their geographical position. A similar parallel with regard to ease of hydrogenation has been found.

The samples, stored under water when received, were filtered, ground to somewhat less than pea size, and dried in a current of Viking natural gas at 110° C. and at a pressure of 25 mm. of mercury. This gas, mostly methane, was dry and free from sulphur. Immediately after drying, the coal was transferred to a ball mill in which it was ground to pass a 100 mesh sieve. The coal was used within 24 hr. of its preparation.

Commercial electrolytic hydrogen, stored in steel cylinders, was used. The catalyst was in every case molybdic oxide prepared by the dehydration of molybdic acid just below dull red heat.

TABLE I

COALS OF 1930 ALBERTA SURVEY

Coal	Geological horizon	Canadian classification	Analysis of pure dry coal, S, etc., omitted			Seyler's classification	Calorific value, B.t.u./lb. pure, moist coal	Ulmins soluble in potash, % of pure dry coal	Fuel ratio FC/VM as received
			C	H	O + N				
A	Kootenay	Semi-anthracite	93 05	4 05	2 90	Ortho-carbonaceous	15,380	0 05	7 5
B	Kootenay	Semi-bituminous	91 40	4 40	4 20	Ortho-carbonaceous	15,560	0 0	5 4
C	Kootenay	Bituminous	88 7	5 20	6 10	Ortho-bituminous	15,380	0 0	2 25
D	Kootenay	Bituminous	87 65	5 60	6 75	Ortho-bituminous	15,490	0 02	1 75
E	Kootenay	Bituminous	85 10	5 55	9 35	Para-bituminous	14,610	0 16	1 70
F	Belly River	Sub-bituminous	83 80	6 05	10 15	Meta-per-lignitous	14,240	1 9	1 19
G	Belly River	Domestic	79 5	5 4	15 1	Ortho-lignitous	12,580	11 5	1 35
H	Edmonton	Domestic	78 95	5 30	15 75	Ortho-lignitous	11,880	47 1	1 32
J	Belly River	Domestic	77 9	5 2	16 9	Ortho-lignitous	11,320	13 6	1 40
K	Belly River	Domestic	77 40	5 15	17 45	Ortho-lignitous	10,370	39 5	1 36
L	Belly River	Domestic	75 40	5 25	19 35	Ortho-lignitous	9,940	49 7	1 50
M	Belly River	Domestic	73 5	5 2	21 3	Lignite	9,250	54 1	1 45
N	Edmonton or younger	Domestic	71 95	5 15	22 9	Lignite	8,420	60 2	1 12

NOTE:—*FC/VM = ratio of fixed carbon to volatile matter.*

TABLE II

COALS OF ALBERTA 1930 SURVEY

Sample	Location	H_2O, as received	Ultimate analysis, dry basis						
			C	H	Ash	S	N	O	C/H
A, 306/30	Anthracite	2.2	80.50	3.50	12.0	1.00	1.1	1.9	23.0
			92.45	4.00	–	0.65	1.3	1.6	23.1
B, 307/30	Canmore	1.4	85.10	4.05	6.0	0.75	1.5	2.6	21.0
			90.65	4.35	–	0.80	1.7	2.5	20.8
C, 303/30	Coleman	1.4	81.35	4.70	7.3	0.45	1.2	5.0	17.3
			88.30	5.15	–	0.45	1.3	4.8	17.1
D, 302/30	Bellevue	1.2	73.45	5.55	15.1	0.60	1.3	5.0	16.1
			87.25	5.60	–	0.45	1.5	5.2	15.6
E, 305/30	Pincher Creek	3.3	76.10	4.75	10.1	1.15	0.7	7.2	16.0
			84.70	5.55	–	0.45	1.2	8.1	15.3
F, 304/30	Lundbreck	4.9	70.55	5.00	13.9	0.85	1.9	7.8	14.1
			83.30	6.00	–	0.60	2.3	7.8	13.9
G, 301/30	Lethbridge	9.8	70.15	4.80	10.8	0.75	1.8	11.7	14.6
			79.10	5.35	–	0.55	1.9	13.1	14.8
H, 308/30	Champion	12.9	70.90	4.80	7.7	0.40	1.3	14.9	14.8
			78.65	5.30	–	0.35	1.3	14.4	14.8
J, 309/30	Taber	15.0	69.95	4.75	8.8	1.10	1.7	13.7	14.7
			77.40	5.15	–	0.65	2.0	14.8	15.0
K, 310/30	Grassy Lake	18.8	67.85	4.65	10.6	1.20	1.4	14.3	14.6
			76.70	5.10	–	0.90	1.9	15.4	15.0
L, 311/30	Winnifred	22.6	68.30	4.40	10.0	0.60	1.3	15.4	15.5
			74.90	5.20	–	0.70	1.4	17.8	14.4
M, 313/30	Redcliff	26.6	67.65	4.35	10.4	0.50	0.8	16.3	15.6
			73.10	5.15	–	0.55	1.1	20.1	14.2
N, 312/30	Eagle Butte	30.3	60.70	3.95	12.2	0.35	1.2	21.6	15.4
			71.65	5.15	–	0.40	1.1	21.7	13.9

NOTE:—*Ultimate analysis—dry basis in first line – dry, ash-free basis, taken from curves, in second line—for each coal.*

Two suspension media were used, tetralin and a paraffin oil fraction of medicinal grade known as liquid petrolatum, B.P. The tetralin was the 1,2,3,4- isomer and of the grade supplied by Eastman (b.p. 202–204° C.). The results of the A.S.T.M. distillation of the liquid petrolatum are given in Table III.

TABLE III

A.S.T.M. DISTILLATION OF LIQUID PETROLATUM

Initial boiling point 152° C.

10% over at 327° C.
20% over at 345° C.
30% over at 357° C.
40% over at 365° C.
50% over at 371° C.
60% over at 376° C.

70% over at 380° C.
80% over at 385° C.
90% over at 395° C.

3½% over at 300° C.
91½% over at 400° C.

The apparatus, consisting of the storage system, autoclave, and auxiliary equipment, has been described in detail (3). Pressure measurements were made with a Bourdon tube gauge calibrated at intervals with a standard test gauge. Temperature measurements, made with a calibrated iron–constantan thermocouple, were indicated on a recording potentiometer controller. The instrument permitted control to within ±5° C.

Gas analyses were made with an improved type of Bureau of Mines apparatus.

Experimental Procedure

Approximately 200-gm. samples of the dry powdered coal were mixed with the desired quantity of suspension medium and 5% by weight of molybdic oxide was thoroughly incorporated with the mixture. One hundred and fifty grams of tetralin was found to produce a sufficiently fluid charge, but 200 gm. of liquid petrolatum was required. The resulting paste was transferred to the autoclave, the weight added being accurately determined, the apparatus sealed gas-tight and, after washing out the air with natural gas, hydrogen added to give the desired initial pressure. Oscillation was started when the autoclave reached a temperature of about 100° C. The reaction mixture reached 425° C. in 2½ to 2¾ hr., and 450° C. in 2¾ to 3 hr. The reaction chamber was maintained at the desired operating temperature for a period of four hours, during which a steady decrease in pressure indicated a corresponding absorption of hydrogen. No attempt was made to counteract the possible catalytic effect of the steel walls of the autoclave.

At the end of the four hour interval, heating was stopped and the autoclave allowed to cool overnight. The residual gases were bled through the expansion valve the following morning and led through activated charcoal absorbers, after which they were measured in an oil-filled wet-test meter before storage in a water-sealed gas holder. The gas was allowed to stand until it was of uniform composition, and a sample was drawn off for analysis. The increase in weight of the charcoal absorbers was noted and the spent absorbent revivified by steam distillation. The yield of condensable products was noted and the gas volume measured in most instances.

The autoclave was recharged with hydrogen and a second cycle completed in a manner identical with that described above. The reaction chamber was then opened and the contents withdrawn as rapidly as possible, weighed and transferred to a glass-stoppered vessel. In spite of the precautions taken the volatile nature of some of the constituents of this mixture resulted in high evaporative losses. The reported oil yield is consequently low in all experiments. In the experiments in which liquid petrolatum was used, a hard brittle coke adhering to the walls of the autoclave and which was removed with difficulty was often encountered. The estimated loss of solid products in such cases was 10 gm

The yield of solid and liquid products was estimated in the following manner. The oily mass from the autoclave was filtered by suction and the residual solids washed with ether and subsequently dried and weighed. The weight of dried coke less the weight of catalyst used thus represented the solid residue from the coal, together with any coke formed in the decomposition of the charge. In this way the oil yield was determined as the difference between the total weight of reaction products extracted from the autoclave and the dried solid residue.

The filtrate from the ether washing was distilled to recover the ether, the distillation residue being added to the oil obtained by filtration. The combined oils were then subjected to distillation analysis. The first fraction, that boiling below 175° C., usually contained a large amount of water. The yields of oil and water were recorded separately. The second and largest fraction was that distilling between 175 and 225° C., and, in the experiments in which tetralin was used, included all the tetralin as well as any decalin or naphthalene formed. The final fraction, taken up to 300° C., was small and included a reddish, viscous oil of evident lubricating value. On occasion wax-like crystals were obtained at about 280° C. The residue from the distillation was a stable pitch boiling at temperatures as high as 450° C. without decomposition. The consistency of the pitch depended upon the coal and the medium used. The pitch was of particular interest in that it closely resembled the residues obtained from distillation analyses of the products of hydrogenation of bitumen from the McMurray bituminous sand deposits (3). The distillation data of oils obtained in the experiments using liquid petrolatum when plotted gave a smooth curve showing no evidence of particular fractions. The water content was lower and the yield of pitch was considerably higher than they were when tetralin was used. The pitch was much softer than that obtained in the tetralin series.

The yield of gaseous products and the hydrogen absorption were calculated from gas analyses and total gas volume data. In estimating the amount of hydrogen absorbed, two procedures were used. In the petrolatum series it was assumed that both the medium and the coal were reduced, but in the tetralin series the absorption of the hydrogen was attributed to the coal alone.

It is uncertain how much hydrogen was absorbed by the medium, but it is probable that it was considerably less with tetralin than in the experiments with petrolatum. Lush (10) has shown that tetralin is the final product of the hydrogenation of naphthalene at much lower temperatures, and Hall (5) has found that little production of low boiling material occurs under comparable conditions up to 400° C. However, Hall found considerable production of low boiling material but little of decalin or naphthalene when tetralin was hydrogenated at 450° C. Hall gives data on hydrogen absorption for naphthalene only, but on the basis of his tabulated pressure changes and gas compositions in comparable experiments with naphthalene and tetralin, the absorption with tetralin is less than one-half that with naphthalene. Comparing with the experiments reported here, a maximum absorption by the medium of 2.5% by weight may occur. Under the more complex conditions obtaining when coal is a competitor for a limited supply of hydrogen, a much smaller absorption of hydrogen by the medium may be expected.

Results and Discussion

Hydrogenation in the Presence of Tetralin

The results obtained in the hydrogenation of the 13 coals are presented in Table IV. For the most part the data will need no interpretation but it will be well to define precisely some of the expressions used.

The amount of hydrogen absorbed is given as percentage by weight of the coal put into the autoclave. The gas yield in litres per kilogram of charge is calculated on the same basis, and is derived from the volume of gas, less hydrogen, removed from the autoclave. The percentages converted to gases, liquids and solid residue are based on the total charge, including the catalyst, and for this reason the figures given for the solid residue recovered include the catalyst. The percentage loss is thus the difference between 100 and the sum of the percentages of the recovered products. The values for the gas analysis are averages of those for each cycle, account being taken of the gas volumes in each case. The figures on total conversions are obtained by subtracting the weight of the solid residue removed from the autoclave, not including catalyst, from the dry coal charged. They thus represent the percentage of the coal converted to oil, gas and water. To calculate the conversion of the coal on the basis of dry, ash-free coal it is necessary only to divide these figures by the difference between one and the fraction of the dry coal that is ash. Conversions on the basis of dry, ash-free coal are consequently higher.

The distillation analyses have been included in order to show the percentage conversion of the total charge to oils in the respective boiling ranges cited. The loss shown at the end of this section represents the distillation losses only. The total oil and water distillate to 300° C. plus the yield of residual pitch, plus the distillation loss, adds up to the total conversion of the charge to liquid products.

The results in Table IV indicate clearly the definite progression in susceptibility to hydrogenation from old to young coals. Numerous small discrepancies will be noted but for the most part these are within the experimental error. The hydrogen absorption increases roughly from 3.9 to 4.4% for anthracite coals to an average value of 6 0% for domestic coals. In this respect Experiment 165 on Coal L-311 represents an interesting departure from the normal. It will be noted that the initial pressure of hydrogen was low. Hence it may be suggested that the extent of reaction depends on the concentration of hydrogen to some extent.

The discrepancy in Experiment 161 on Coal J-309 is not large and probably within experimental error. The remaining experiments fall into a fairly normal progression from the point of view of hydrogen absorption.

In agreement with this tendency to increased hydrogen absorption, an inspection of the pressure–time relations indicates that the rate as well as the amount of hydrogen absorption also increases as the age of the coal decreases. In Fig. 2, the pressure–time relations are given for the first cycles of experiments conducted with representative coals of various rank. The temperature reached 450° C. in about three hours or less. The rate of

TABLE IV

HYDROGENATION OF ALBERTA COALS IN THE PRESENCE OF TETRALIN

Experiment number	146	148	151	171	155	144	157	159	161	163	165	167	169
Sample number	A-306	B-307	C-303	D-302	E-305	F- 304	G-301	H-308	J-309	K-310	L-311	M-313	N-312
Weight of coal, gm.	186	195	185	194	191	200	204	200	189	193	194	195	199
Weight of tetralin, gm.	144	146	138	146	144	132	149	148	144	145	146	151	147
Average initial pressure, lb./sq. in.	960	940	995	1015	1000	920	1000	990	1045	1000	790	970	1030
Average maximum pressure, lb./sq. in	2545	2500	2595	2620	2570	2525	2665	2855	2950	2785	2570	2715	3195
Average final pressure, lb./sq. in.	660	595	525	530	510	450	475	505	585	485	410	510	545
Average pressure drop, lb./sq. in.	300	345	470	385	490	470	525	485	460	515	380	460	485
Hydrogen absorbed, %	3.9	4.4	6.0	5.7	5.3	5.5	5.8	5.6	5.5	6.2	4.5	5.6	5.9
Gas yield, less H_2, l./kg. of charge	76.8	74.8	110.8	98.8	75.7	117.0	100.0	111.0	85.3	113.8	96.0	105.6	119.0
Charge to liquids, %	35.5	46.8	69.0	69.5	67.7	60.2	65.5	61.2	65.4	66.0	64.5	65.0	64.3
Charge to solid residue, %	52.4	41.3	23.5	18.6	16.9	15.7	14.7	14.4	11.5	11.6	13.2	10.8	10.8
Charge to gas (including gas from charcoal), %	6.0	6.7	8.5	8.4	7.8	9.9	9.4	11.2	12.3	11.0	9.6	10.2	10.8
Charge to loss, %	6.1	5.2	0.0	3.5	7.6	14.2	10.4	13.2	10.8	11.4	12.3	14.0	14.1
Gas analysis, %													
CO_2	0.2	0.2	2.2	1.0	0.4	1.3	2.9	4.4	3.9	4.2	7.3	7.2	8.8
C_nH_{2n}	0.4	0.4	0.4	0.5	0.5	0.6	0.7	0.2	0.1	0.1	0.3	0.1	0.3
H_2	77.3	74.5	60.9	63.4	72.0	52.4	56.5	57.5	71.5	54.5	56.2	57.5	56.6
CO	0.6	0.6	1.7	0.7	1.0	1.4	1.9	1.1	1.2	3.2	1.6	2.0	2.1
C_2H_6	4.5	5.5	8.7	9.7	7.2	13.1	14.7	12.0	9.0	24.8	10.8	10.9	11.3
CH_4	9.9	12.1	16.0	12.7	11.0	25.2	14.3	27.7	25.8	16.1	19.0	21.0	20.2
Coal converted (dry coal), %	10.8	32.3	64.6	73.5	77.0	80.0	80.5	81.3	86.4	86.3	83.0	87.7	88.0
Coal converted (dry, ash-free coal), %	12.2	34.9	72.3	85.0	87.0	92.0	90.7	89.3	95.1	95.7	91.2	96.7	96.2
Charge to volatile products absorbed in charcoal, %	2.3	2.8	3.0	3.4	3.7	2.6	3.3	3.3	3.8	3.7	3.7	3.3	3.1
Charge to oil, %.—(1) Oil to 175° C.	3.6	3.6	5.4	6.1	3.6	10.8	7.3	6.8	6.7	7.9	7.2	7.1	7.4
(2) Oil to 225° C.	27.7	30.4	41.9	43.1	37.6	37.9	34.7	36.0	39.1	36.7	36.6	37.5	37.0
(3) Oil to 300° C.	30.0	32.3	45.0	49.5	45.4	44.5	43.2	42.7	46.6	46.5	43.8	46.5	44.8
(4) Pitch	5.5	14.5	23.7	19.4	20.7	14.2	15.9	13.2	14.6	10.6	12.0	12.3	9.6
(5) Water	0.0	0.0	0.3	Trace	1.3	0.6	6.3	5.0	4.2	7.9	8.7	5.6	8.7
(6) Loss	0.0	0.0	0.0	0.6	0.3	0.9	0.0	0.3	0.0	0.0	0.0	0.6	1.2

reaction some time after hydrogenation has begun is indicated by the downward slope of the curve, and the total drop in pressure is a rough measure of the amount of hydrogen absorbed. Thus, for an anthracite coal the rate of reaction is low and the total absorption is small. For bituminous and sub-bituminous coals the rate of reaction appears to be much the same, but the younger coal exhibits a much greater absorption. The extremely rapid absorption of hydrogen by domestic coals is clearly illustrated in the fourth curve.

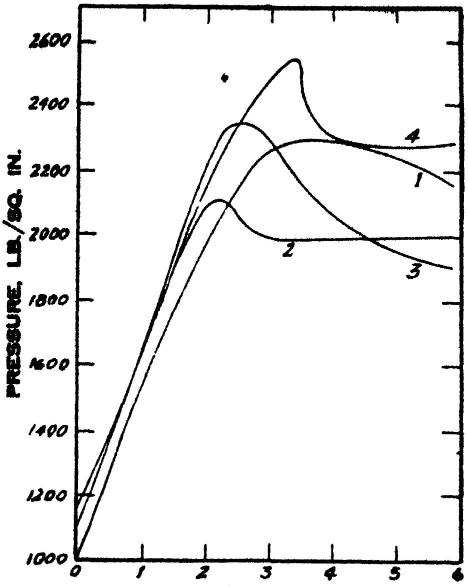

Fig. 2. *Pressure-time relations, first cycles, tetralin medium. 1–Semi-anthracite, A; 2–bituminous, C; 3–sub-bituminous, G; 4–domestic, J.*

A similar analysis was made of the pressure–temperature relations in these four experiments and it was noted that the temperature at which hydrogenation begins, as shown by changing curvature and heat evolution, decreased regularly from about 400° C. for semi-anthracite to less than 300° for domestic coal. Layng (9) has pointed out that a decrease in the temperature of plasticity of coals becomes apparent when the coals are arranged in descending order of maturity. The exact relation of temperature of plasticity and the initial stages of hydrogenation has received the attention of Arend (1).

Fig. 3 presents the pressure–time relations of the second cycle of experiments on the same four coals with which the results shown in Fig. 2 were obtained. It will be noted that a higher temperature is required for hydrogenation to take place when a coal has previously been attacked by hydrogen. Apparently the less stable constituents become hydrogenated in the first cycle. It is further evident from these curves that the residues after the first cycle are more nearly alike than were the

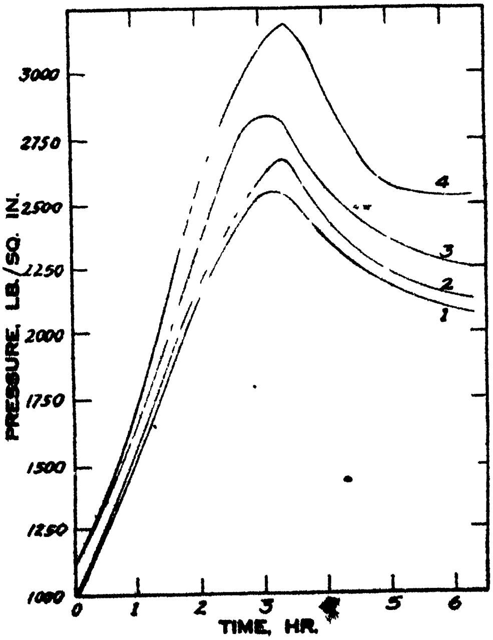

Fig 3. *Pressure-time relations, second cycle, tetralin medium. Coals as in Fig. 2.*

original coals. This evidence is of importance in the application of hydrogenation to a continuous process. It appears that under the conditions most suitable for partial hydrogenation of fresh material the reaction is not complete, and more drastic conditions are necessary to obtain further reduction. The use of a higher temperature in the first cycle would lead to the formation of excessive amounts of gas and coke. Thus the evidence shows that satisfactory results, with particular regard to speed of reaction, would be obtained in continuous operation if apparatus designed for successive treatments at higher temperatures were used.

A further inspection of Table IV shows a definite increase in gas production as the coals decrease in age. Coincident with this is the tendency toward the development of higher maximum pressures. Analysis of the exit gases shows a pronounced increase in the carbon dioxide and carbon monoxide yields. The extent to which the coals became oxidized during milling and storing is difficult to estimate. The susceptibility to oxidation that is characteristic of young coals may account, in some measure, for the increased production of oxygenated compounds.

Paralleling this tendency to increased yields of carbon monoxide and carbon dioxide, the formation of water takes place to a greater extent with younger coals. It is probable that water is formed by reduction and decomposition of oxygen-containing groups such as hydroxyl in the coal. This subject will be more fully discussed later.

From Table IV it is further apparent that there is a general tendency toward increased mechanical losses with decrease in age of the coals. This may be taken as indicating an increasing conversion to low-boiling oils. Appreciable amounts of propane, butane and other volatile hydrocarbons appeared in the charcoal absorbers, and this, with the excessive amounts of carbon dioxide formed in the combustion analyses of the residual gases, further supports this view.

Though numerous small discrepancies are apparent there is a tendency toward a decrease in residual hydrogen with decreasing maturity of the coals.

In general the relative conversions to light oil, gas and water increase at the expense of the pitch formation, with decreasing maturity of the coals.

Two experiments on domestic coals (Experiments 165 on L-311 and 167 on M-313) were characterized by the appearance of considerable naphthalene in the reaction products. This would suggest that the reaction was incomplete after eight hours of operation. As has been previously mentioned, the initial hydrogen pressure in Experiment 165 was quite low. The formation of naphthalene in spite of the appreciable quantity of hydrogen present indicates the effective reducing action of tetralin.

Fractionation of the 175-225° C. fraction was carried out in a few cases with the lower-rank coals. Between 192 and 215° C. at 700 mm. pressure there was a halt in the temperature–volume curve while 60% to 70% of the fraction came over, the last portions being naphthalene. Assuming this material to be tetralin, decalin and naphthalene, the recovery of medium was between 40 and 50% of the initial quantity used. The loss may be assigned to the decomposition of tetralin into low-boiling products.

A study of the data from the point of view of oil yield alone suggests that low grade bituminous or sub-bituminous coals are the most suitable for the process. The ease of hydrogenation and lower cost of domestic coals may be so favorable, however, as to make them the more suitable coals in spite of the higher water and gas production. The evidence is not conclusive.

Hydrogenation in the Presence of Liquid Petrolatum

Though the behavior of the coals upon hydrogenation in a liquid petrolatum medium was in general the same as that in tetralin, the conversions and general efficiency of the process were definitely poorer.

The results of this series of experiments are shown in Table V. The lines have the same significance as in Table IV, excepting "Hydrogen absorbed". It will be noted, however, that larger amounts of suspension medium were used, and that the hydrogen absorption was lower than that with the tetralin. This is due in part to the method of calculation, in which the whole charge was considered. Furthermore, these experiments were made at 425° C. as compared with 450° with tetralin. The reason for this lies in the greater stability of tetralin to heat. Extensive decomposition of liquid petrolatum takes place at 450° C. with the formation of gas and coke. It was not possible to determine what part of the gas and solid residue production in these experiments could be attributed to the medium.

An inspection of the table shows the expected increase in gas production and in maximum reaction pressures with decrease in maturity of the coal. The exception in Experiment 152 on Coal C-303 cannot be explained on the grounds of technique. The exit gas was unusually low in hydrogen. The excessive gas yields in Experiments 164 with Coal K-310 and 166 with Coal L-311 may be attributed to a higher temperature of operation. The former experiment got out of control and the temperature rose to 440° C. for a short time. Experiment 166 was also out of control and the temperature rose momentarily to 470° C. and was greater than 430° for 45 min. The excessive coke yield and low conversion to liquids that occurred in this experiment may also be attributed to the high operating temperature. More reliable data regarding the coal may be obtained from Experiments 163 and 165 of the tetralin series.

From Table V the same conclusions regarding high evaporation losses and high conversion to low-boiling oils and water may be drawn as in the tetralin series. It will be noted that in general the formation of water in this series of experiments is decidedly lower than that in the tetralin series, but the carbon dioxide formation is much the same.

TABLE V

HYDROGENATION OF ALBERTA COALS IN THE PRESENCE OF LIQUID PETROLATUM

Experiment number	147	149	152	154	156	145	158	160	162	164	166	168	170
Sample number	A-306	B-307	C-303	D-302	E-305	F-304	G-301	H-308	J-309	K-310	L-311	M-313	N-312
Weight of coal, gm.	197	194	191	195	190	179	193	194	188	189	195	193	196
Weight of solvent, gm.	197	204	191	205	201	179	195	200	193	189	195	194	199
Average initial pressure, lb./sq. in.	920	880	990	1030	1015	985	970	985	1015	1005	970	995	970
Average maximum pressure, lb./sq. in.	2195	2080	2380	2405	2480	2525	2500	2480	2645	2670	3050	2740	2950
Average final pressure, lb./sq. in.	725	660	570	645	610	570	510	605	555	565	610	565	575
Average pressure drop, lb./sq. in.	195	220	420	385	405	415	460	380	460	440	360	430	395
Hydrogen absorbed, %	1.0	1.4	2.6	2.1	2.2	2.5	2.5	2.5	2.6	2.6	2.4	2.5	2.4
Gas yield, less H_2 in l./kg. of charge	37.5	40.4	116.2	45.2	65.0	71.5	79.5	82.5	66.0	92.5	137.0	78.3	87.0
Charge to liquids, %	38.5	44.6	49.5	54.0	57.2	59.6	53.2	56.8	57.8	59.8	41.3	56.7	64.3
Charge to solid residue, %	48.5	46.8	33.0	33.7	28.8	28.5	25.8	23.0	22.8	22.4	30.0	25.1	16.7
Charge to gas and charcoal, %	5.4	5.7	9.1	4.9	7.6	7.8	8.8	10.1	7.3	10.2	16.0	8.6	9.0
Charge as loss, %	7.6	2.9	8.4	7.4	6.4	4.1	12.2	10.1	12.1	7.6	12.7	9.6	10.0
Gas analysis, %													
CO_2	0.2	0.3	6.3	0.3	0.4	0.6	2.7	4.3	3.6	4.8	7.6	6.5	9.0
C_nH_{2n}	0.3	0.3	0.2	0.4	0.3	0.5	0.5	0.5	0.1	0.2	nil	0.3	0.2
H_2	87.0	83.5	52.8	81.5	74.8	73.7	65.4	63.5	71.8	62.5	53.7	67.6	62.8
CO	0.4	0.2	2.9	0.4	1.4	1.3	1.0	1.6	1.2	3.0	2.7	2.3	2.0
C_2H_6	3.8	1.6	6.7	3.3	3.7	6.8	11.3	13.7	7.8	12.1	27.8	9.3	10.4
CH_4	2.4	8.7	15.7	7.3	12.0	11.9	10.0	13.2	14.4	18.8	11.5	10.8	13.5
Coal converted (dry coal), %	7.1	9.3	40.8	37.7	47.9	50.3	55.6	61.0	61.8	63.0	46.9	57.5	74.6
Coal converted (dry, ash-free basis), %	8.0	10.1	45.6	43.6	54.2	57.7	62.6	66.9	68.1	69.9	51.4	63.4	81.6
Charge to volatile products absorbed in charcoal, %	3.7	3.8	4.0	2.9	4.6	3.2	4.2	4.4	3.0	4.3	3.7	3.7	3.4
Charge to oil, %.—(1) Oil to 175° C.	6.6	7.8	12.8	9.1	8.2	11.7	9.9	13.0	9.4	12.6	11.8	9.4	10.7
(2) Oil to 225° C.	12.6	12.0	21.0	15.0	15.9	20.7	19.2	22.5	17.0	22.1	19.2	16.3	17.5
(3) Oil to 300° C.	20.2	20.1	32.7	25.4	26.7	34.0	29.3	33.0	28.7	32.5	26.9	29.3	30.5
(4) Pitch	18.3	23.9	15.4	28.6	28.1	23.4	20.0	20.0	25.2	22.4	9.1	23.8	24.6
(5) Water	0.0	0.0	1.4	0.0	1.9	2.2	3.9	3.5	3.6	4.6	5.0	3.3	7.1
(6) Loss	0.0	0.6	0.0	0.0	0.5	0.0	0.0	0.3	0.3	0.3	0.3	0.3	2.0

Figs. 4 and 5 represent the pressure–time relations of the first and second cycles of experiments conducted with four typical coals, three of which correspond to those with which the results shown in Figs. 2 and 3 were obtained. It will be seen that again hydrogen absorption is greatest and most rapid with domestic coals. Sub-bituminous and bituminous coals exhibit appreciable absorption, though the reaction rate is lower than that of domestic coals, and the slight effect of hydrogen on anthracite coal is again brought out.

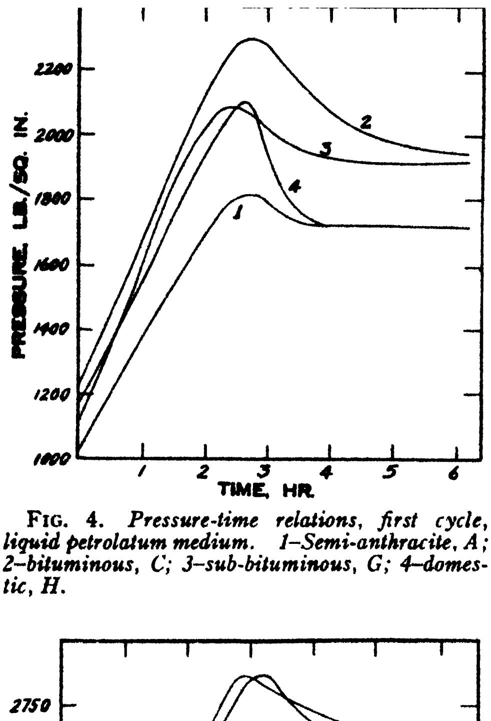

FIG. 4. *Pressure-time relations, first cycle, liquid petrolatum medium. 1–Semi-anthracite, A; 2–bituminous, C; 3–sub-bituminous, G; 4–domestic, H.*

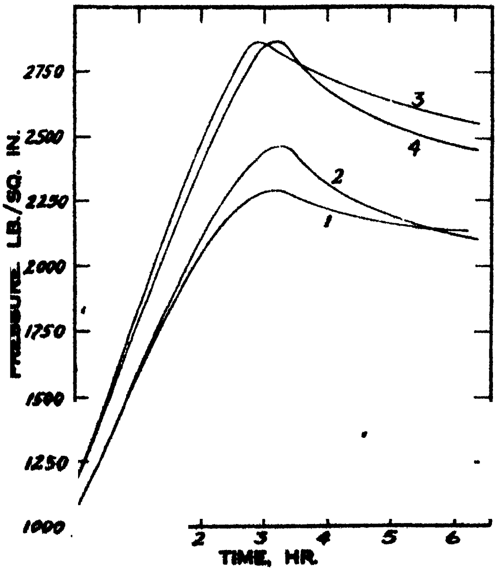

FIG. 5. *Pressure-time relations, second cycle, liquid petrolatum medium. Coals as in Fig. 4.*

Yields of oil, gas and water as high as 75% from a domestic coal under the conditions employed indicate that heavy petroleum oils such as liquid petrolatum might be suitable vehicles in which to suspend the coal. It is to be expected that conditions, differing for each coal, could be found such that higher conversions would take place, but the procedure in this investigation was standardized so as to form a basis for comparison of the coals studied

As was the case with the tetralin series, the evidence of these experiments suggests bituminous or lower grade coals as most suitable for the process. A definite choice requires a study of costs, and additional experiments for the purpose of ascertaining optimum conditions for each grade of coal.

Comparison of Tetralin and Liquid Petrolatum as Suspension Media

The definite superiority of tetralin as a suspension medium for coal is shown by higher hydrogen absorption and lower coke formation than occurs in the petrolatum series.

Carbon dioxide production is much the same with both solvents, indicating no special tendency of tetralin to aid in the decomposition of carboxyl groups in the coal. Water formation is definitely greater in the tetralin series and indicates reduction of oxygenated compounds which are not reduced by hydrogen with a liquid petrolatum medium.

The formation of ammonia in certain experiments in which tetralin was used indicated the reduction of nitrogenous material, whereas the absence of ammonia as a product of reaction in any of the experiments of the petrolatum series showed that a milder reduction had taken place. Ammonia formation in the tetralin may be due, however, at least in part, to the higher operating temperature employed. A comparison of the two media may be made from the data of Table VI.

TABLE VI

COMPARISON OF LIQUID PETROLATUM AND TETRALIN AS SUSPENDING MEDIA

Coal	Liquid petrolatum			Tetralin		
	Oils and gas	Water	Total	Oils and gas	Water	Total
Conversions on basis of dry coal						
A	7.1	0.0	7.1	10.8	0.0	10.8
B	9.3	0.0	9.3	32.3	0.0	32.3
C	38.0	2.8	40.8	64.1	0.5	64.6
D	37.7	0.0	37.7	73.4	0.1	73.5
E	44.1	3.8	47.9	74.7	2.3	77.0
F	45.9	4.4	50.3	79.0	1.0	80.0
G	47.8	7.8	55.6	69.7	10.8	80.5
H	53.9	7.1	61.0	72.6	8.7	81.3
J	54.5	7.3	61.8	79.0	7.4	86.4
K	53.8	9.2	63.0	72.9	13.4	86.3
L	36.9	10.0	46.9	67.8	15.2	83.0
M	50.9	6.6	57.5	77.7	10.0	87.7
N	60.3	14.3	74.6	72.9	15.1	88.0
Conversions on basis of dry, ash-free coal						
A	8.0	0.0	8.0	12.2	0.0	12.2
B	10.1	0.0	10.1	34.9	0.0	34.9
C	42.5	3.1	45.6	71.7	0.6	72.3
D	43.6	0.0	43.6	84.9	0.1	85.0
E	49.9	4.3	54.2	84.1	2.9	87.0
F	52.7	5.0	57.7	90.9	1.1	92.0
G	53.8	8.8	62.6	78.6	12.1	90.7
H	59.1	7.8	66.9	79.7	9.6	89.3
J	60.1	8.0	68.1	86.9	8.2	95.1
K	59.9	10.0	69.9	80.5	15.2	95.7
L	40.4	11.0	51.4	74.5	16.7	91.2
M	56.1	7.3	63.4	85.7	11.0	96.7
N	66.0	15.6	81.6	79.9	16.3	96.2

The columns in Table VI are self-explanatory and the data serve to show quite clearly the effects of the two media. A rapid comparison may be made by consulting Fig. 6, in which the degree of hydrogenation is shown graphically. In this diagram the conversion of coal in all cases represents percentage converted to gas, oil and water, and is calculated from the residual solid material. The large discrepancy in the results for Coal L in the petrolatum series has been mentioned earlier, and is due to the high temperature at which hydrogenation took place.

The ultimate analyses of the dry, ash-free coals also have been recorded in Fig. 6. It will be seen that, in general, the extent of hydrogenation parallels roughly the oxygen content of the coal, and changes inversely with the carbon content. This fact was recognized by Bergius (2), who, in this connection, predicted that coals containing more than 85% carbon were not amenable to hydrogenation. Thus, of this series, Coals A-E inclusive should not be susceptible to hydrogenation. However, it was found that Coals C, D and E were quite susceptible to hydrogenation and appreciable reduction of Coals A and B also occurred.

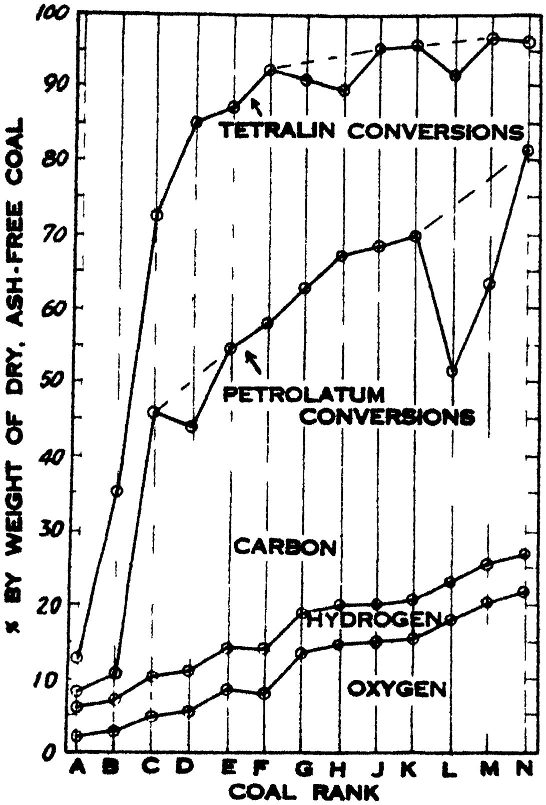

Fig. 6. *Coal conversion, rank, and ultimate analysis on dry ash-free basis.*

The effective action of tetralin as a medium compared to other substances has been attributed previously (3) to a hydrogen carrying action. These earlier results showed clearly that tetralin can hydrogenate coal in the absence of free hydrogen, with the resulting formation of naphthalene. In fact, naphthalene is produced in amounts that increase with a decreasing supply of gaseous hydrogen. It is reasonable to assume that the mechanism is the same in all cases, that the tetralin hydrogenates the coal and that the hydrogen reduces the resulting naphthalene to tetralin.

It has been fairly well established that, in destructive hydrogenation processes, four reactions predominate; a thermal decomposition of complex bodies to form unsaturated fragments, a hydrogenation or stabilization of these fragments, a decomposition and polymerization of these fragments to form coke and gas and hydrogenation of phenolic bodies with the production of water. Waterman and Perquin (13, 14) in working with paraffin wax were led to the theory that the function of the hydrogen was, primarily, that of stabilizing unsaturated fragments by prevention of dehydrogenation. The fragments were themselves stable. Kling and Florentin (8) and Tropsch (12) do not support this and suggest that the hydrogen reduces the unsaturated fragments to form saturated stable bodies. The hydrogenation equilibrium is favored by low temperatures, and the decomposition and polymerization reactions resulting in coke and gas formation are favored by high temperatures. Moreover, the latter reactions tend to go to completion (7, 14). The function of the catalyst may be said to be the promotion of decomposition at low temperatures at which hydrogenation can proceed to an extent sufficient to reduce all or most of the unsaturated fragments.

The evidence of the work in this laboratory on tetralin and other media is in substantial agreement with the second mechanism. A significant modification in the mechanism is suggested, however. It is suggested that the function of the medium is the reduction of the unsaturated fragments or bodies, and the function of the hydrogen is the maintenance of the medium in the reduced state.

The Oxygenated Compounds in the Hydrogenation of Coal

Parr and Hadley (11) investigated the oxidation of coal and found that the combined oxygen was liberated as carbon dioxide upon thermal decomposition of the coal. It is thus reasonable to suppose that carbon dioxide is a product, to some extent, of thermal decomposition rather than of the specific action of hydrogen. This would account for the production of carbon dioxide in comparable amounts in the two series of experiments.

The formation of water is due in a large measure to hydrogenation of phenolic bodies in the coal (12). Examination of Table VI reveals that in general water is produced to a greater extent in the tetralin series. Two theories may be suggested to account for this.

Increased water formation in the tetralin series may be attributed to the higher temperature of operation throughout, resulting in a decreased stability of the phenolic substances. This theory is substantiated by the excessive water yields reported in those experiments of the petrolatum series in which the temperature of the reaction chamber rose above 430° C. For example, Experiment 164 with Coal K-310 was out of control and the temperature rose to 442° C. The water yield in this case was 4.6%. In Experiment 166 with Coal L-311 the temperature rose to 470° C. and the yield of water was 5.0%. Experiments with other domestic coals resulted in water yields averaging 3.5% (neglecting Coal N-312, of lignitic character). In these experiments the temperature did not rise above 430° C.

The alternative theory may be stated with some evidence in its favor. It is the view that excessive water yields are produced by hydrogenation of phenolic bodies which would otherwise remain unattacked, the action being attributed to the efficient manner in which tetralin itself will act as a hydrogenating agent. In view of the fact that operation at 450° C. caused a water yield of 8.7% in Experiment 165 on Coal L-311 of the tetralin series, a yield much higher than the 5.0% reported in the corresponding liquid petrolatum experiment in which the temperature reached 470° C., it may be concluded that tetralin has a specific action.

It is probable that both temperature and medium affect the water yield. Unfortunately, definite information would depend on experiments which have not been made, *viz.*, experiments involving equal temperatures of operation for the two media, and ultimate analyses.

The mechanism of reactions involving the production of carbon monoxide is more obscure, and no justifiable conclusions may be drawn from the data presented. It may be remarked, however, that reduction of carboxyl groups by successive stages would produce aldehydes which, according to Hurd (6), decompose readily to give carbon monoxide and a hydrocarbon. Such a source is not improbable and would fit the observed facts.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XII. METHANOL LIGNIN[1]

By Fritz Brauns[2] and Harold Hibbert[3]

Abstract

Methanol lignin was prepared by extracting spruce wood meal with absolute methyl alcohol, using hydrochloric acid as catalyst. In five small, bomb-tube experiments, methanol lignin preparations having the same methoxyl content (about 21.6%) were obtained, the product in each case being apparently homogeneous. The methanol lignin was acetylated, partially methylated by treatment with diazomethane, and fully methylated with dimethyl sulphate and sodium hydroxide. From the elementary analyses and the ratio of methoxyl in the original methanol lignin to that in the diazomethane-methylated compound a formula for the smallest building unit of the methanol lignin and for the native lignin can be derived The latter is represented by the empirical formula $C_{47}H_{52}O_{16}$, or, expanded, $C_{42}H_{32}O_6(OCH_3)_5(OH)_5$

Introduction

The method of isolating lignin from wood by means of hydroxylic compounds in presence of catalysts, such as hydrochloric acid, has been used by a number of investigators during the past 15 years. Gruss (11, 12) was apparently the first to show that lignin could be isolated from wood by heating the latter with alcohol and hydrochloric acid. Later, Hägglund (13–15) applied this same principle, and using a variety of alcohols (methyl, ethyl, amyl) claimed to show that the resulting lignin derivatives were "acetal" derivatives, although no definite proof of this theory was submitted.

Hibbert and co-workers (16, 17) carried out a series of investigations on "glycol lignin" and "glycol monomethyl ether lignin" in which the extraction media were glycol and glycol monomethyl ether respectively. The first method was used independently by Rassow (18–20), and the second, by Fuchs (9). Friedrich and co-workers (7, 8) and Campbell (3) employed ethyl alcohol as the extraction medium. In all cases a product is obtained which contains, depending on the solvent used, the alkyl or the aryl group in ether-like combination with the lignin. In the case of both the lower aliphatic alcohols and of glycol or glycol monoalkyl ethers, the methoxyl value as determined by the standard procedure is influenced by the presence of these groups; on the other hand, the use of phenol as extraction medium gives rise to more complicated lignin derivatives formed as the result of nuclear condensation of the phenol with the lignin molecule (2). In view of this, it seemed advisable to investigate further the use of methyl alcohol as proposed previously by Friedrich (7, 8). The reaction between the methyl alcohol and lignin would be indicated by the higher value of the methoxyl content. The mechanism of the reaction is not clear (4, p. 125).

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Hägglund (13) has suggested that the products are acetals. Since, however, they do not undergo hydrolysis with dilute mineral acids, it is evident that this view is incorrect. In an earlier investigation (10, 16) it was found that, on extracting spruce wood meal with ethylene glycol monomethyl ether, the methoxyl content of the resulting lignin derivative, calculated on the basis of a molecular weight of about 850, had increased by an amount corresponding to approximately one methoxyl group, thus indicating that at least one molecule of glycol monomethyl ether had reacted with the lignin.

As shown in the present paper, extraction of spruce wood meal with absolute methanol yields a methanol lignin in which an additional methoxyl group has been introduced, so that on treatment with hydriodic acid an additional amount of methyl iodide is evolved.

When bone-dry wood meal, previously freed of fats, waxes, resins and water-soluble carbohydrates, is heated in a bomb tube with methyl alcohol containing 2% of hydrogen chloride in a tilting-oven at 85–90° C. for about 100 hr., 50% of the wood meal dissolves and from this a methanol lignin with a methoxyl content of 21.6% can be isolated. Lignin which has been isolated according to Freudenberg's method (5, 6) and which may be considered as closely related to unchanged native lignin, has a methoxyl content of 17.4% (4, p. 125). The increase of approximately 4% in the methoxyl content of methanol lignin, as compared with the methoxyl content of Freudenberg lignin, would seem to be due to the entrance of new methoxyl groups into the lignin molecule as a result of the reaction between the lignin and the methanol.

Methanol lignin is soluble in sodium hydroxide solution, from which it is reprecipitated on the addition of a mineral acid or even carbon dioxide, indicating the presence of a phenolic hydroxyl group. This is confirmed by the behavior of the methanol lignin towards diazomethane. On treatment with this reagent in dioxane solution a strong evolution of nitrogen takes place. The solution changes in color from dark brown to a light brownish-yellow, and a methylated product insoluble in sodium hydroxide and having a methoxyl content of 24.8% is formed. In addition to this weakly acidic hydroxyl group, other hydroxyl groups are present as shown by the acetylation of the original methanol lignin and of its diazomethane-methylated derivative. The acetyl derivatives are no longer soluble in alkali solution.

The presence of free hydroxyl groups in methanol lignin is also shown by the formation of a methylated derivative on treatment with dimethyl sulphate and sodium hydroxide, the fully methylated methanol lignin formed by this treatment having a methoxyl content of 32.3%.

Based on the original methoxyl values of the methanol lignin (21.6%) and the diazomethane-methylated product (24.8%), the number of methoxyl groups in the smallest lignin building-unit can be calculated if it be assumed that only one methoxyl group is formed as a result of methylation with diazomethane. If x represents the molecular weight of the original methanol lignin and y the number of the methoxyl groups, the percentage of methoxyl is given by

$$\frac{31.02 \times y \times 100}{x} = 21.6,$$

and for the diazomethane-methylated methanol lignin the value is represented by

$$\frac{31.02\,(y + 1) \times 100}{x + 14} = 24.82,$$

from which y is found to be 6.05, and x to be 861.

In other words, methanol lignin contains (on the basis of one new methoxyl group formed by the action of diazomethane) six, and the diazomethane-methylated product seven, methoxyl groups, a result in agreement with that shown in an earlier paper (1). It must, however, be emphasized that these calculations are based on the assumption that the original methanol lignin is a homogeneous product. In the bomb-tube experiments described below, in which only small amounts could be prepared, a *single* product only, insoluble in ether, was obtained. Owing to lack of sufficient material no other fractionation experiments could be carried out. As will be shown in a later paper, however, when methanol lignin is prepared on a larger scale in an autoclave, the crude methanol lignin can be separated into two fractions, namely, an ether-insoluble and an ether-soluble, having methoxyl contents of 21.5 and 24.4% respectively. A detailed examination of the two products, their acetylated diazomethane-methylated and fully methylated compounds, is at present being carried out with the object of obtaining more precise information regarding the size of the methanol lignin building-unit.

The formula for methanol lignin is therefore, as shown in the earlier paper, $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OCH_3)$, and for native lignin, $C_{42}H_{32}O_6(OCH_3)_5(OH)_5$.

Experimental

Preparation of Methanol Lignin

Spruce wood meal (25 gm., 100 mesh), dried to constant weight under reduced pressure at 50° C. over phosphorus pentoxide, was heated in a sealed glass bomb tube with 200 cc. of absolute methanol containing 2% of anhydrous hydrochloric acid in a tilting oven at 90–100° C. for 80 hr. The tube was cooled to −15°C. When the tube was opened, a pronounced evolution of gas, presumably methyl chloride, or dimethyl ether, was observed. A slight smell of formaldehyde was also detectable. The reaction product was centrifuged, the residual wood meal washed with a mixture of acetone and methanol (1 : 1) and dried in a desiccator over sulphuric acid. The weight was 12.3 gm., indicating that 50% of the original wood meal had been dissolved. The combined methanol and acetone solutions were concentrated under reduced pressure to a volume of about 20 cc. and then added dropwise in a very fine stream to 500 cc. of well stirred distilled water containing a trace of sodium bicarbonate. The lignin precipitated, in general, as a flocculent material but occasionally remained in colloidal solution. In the latter case it was stirred with a few drops of concentrated sodium sulphate solution which brought about coagulation. The methanol lignin was separated by centrifuging, and finally by filtering through a Büchner funnel. It was washed with distilled water until it was free from sulphate and no longer reduced Fehling's solution. The slimy, chocolate-brown colored product was dried in a desiccator over sulphuric acid. Yield, 1.8 gm. or 25% of the total lignin present in the original spruce meal. Analysis of the product from three different experiments gave OCH_3, 22.0, 21.8, 21.6%, respectively.

Purification of the Methanol Lignin

The methanol lignin was dissolved in sufficient anhydrous dioxane to form a 10% solution and then reprecipitated by adding the solution dropwise to vigorously stirred anhydrous ether. The product was washed twice with ether, then three times with petroleum ether, allowed to stand overnight in the final petroleum ether wash liquor, filtered, and dried in a desiccator over sulphuric acid. A sample for analysis was dried over phosphorus pentoxide at 2 mm. and 110° C. to constant weight. Found: OCH_3, 21.5%. This product was again purified from dioxane and ether. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$, [886.4]:—C, 64.9; H, 6.1; OCH_3, 21.0%. Found: C, 65.12, 65.25; H, 6.02, 6.14; OCH_3, 21.6%.

Methanol lignin is a finely divided buff-colored powder, soluble in dioxane, acetone, methyl and ethyl alcohols, and in dilute sodium hydroxide. It is precipitated from the last-named solution by mineral acids and also by carbon dioxide.

The mother liquor from the methanol-water precipitation was evaporated under reduced pressure to a thick syrup. This was dissolved in distilled water, the small amount of pale brown precipitate which separated out removed by filtration through charcoal, and the aqueous solution evaporated under reduced pressure. The yellowish brown syrup finally obtained was then dried in a vacuum desiccator for several days over solid sodium hydroxide. About 10 gm. of the yellowish brown syrup was obtained in each experiment. This product reduced Fehling's solution only slightly but very strongly after hydrolysis with dilute hydrochloric acid. In the latter case a slight brown flocculent precipitate separated out. After it had been filtered and dried its methoxyl content was 17.5%.

The dioxane-ether mother liquor obtained from the first purification of the methanol lignin was only slightly colored. The solvent was removed by evaporation under reduced pressure, the brownish residue dissolved in about 2 cc. of dioxane and this solution added dropwise to well stirred petroleum ether. Only a very slight precipitate was obtained. This was not investigated further.

The residual methanol-extracted wood meal from three such experiments, representing 50% of the original wood meal used, was dried and analyzed for methoxyl, lignin and cellulose. The methoxyl content, 6.11%, is nearly

50% higher than that of the original wood meal (4.4%), indicating that during the extraction with methyl alcohol and hydrogen chloride a partial methylation had taken place.

A lignin determination showed 26.9% as compared with 29.4% prior to extraction, and a cellulose content of 66.9% was found, as compared with 58.6% in the original wood meal. An extraction of methanol lignin carried out in an open flask at 66° C. resulted in a poorer yield of a crude methanol lignin (OCH_3, 22.7%).

Acetylation of Purified Methanol Lignin

One gram of purified methanol lignin (OCH_3, 21 6%) was dissolved in a mixture of 5 cc. of dry pyridine and 3 cc. of acetic anhydride; the product was allowed to stand at room temperature for 48 hr., and then poured on to ice. The brown precipitate was filtered, washed and dried over sodium hydroxide and sulphuric acid in a vacuum desiccator. It was then dissolved in dioxane, and the solution was centrifuged, filtered and the lignin precipitated by adding the solution dropwise to well stirred anhydrous ether. It was purified further by dissolving it in dry benzene and adding the filtered solution drop by drop to petroleum ether (60–70° C.) with vigorous stirring. The precipitated product was washed first with petroleum ether (b.p. 60–70° C.) then with low-boiling petroleum ether (b.p. 30–50° C.). The product isolated by centrifuging was dried in a vacuum desiccator over sulphuric acid. Yield, 1 2 gm. Prior to analysis it was dried in an Abderhalden oven at 78° C. and 2 mm. to constant weight. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCOCH_3)_4$, [1054 5]:—C, 63 9; H, 5 9; OCH_3, 17 6%. Found:—C, 64.46, 64.20; H, 5.65, 5.77; OCH_3, 17 8%. The acetylated methanol lignin is soluble in benzene, acetone, dioxane and methyl and ethyl alcohols, but insoluble in ether, petroleum ether, water and dilute sodium hydroxide solution.

Methylation of Methanol Lignin with Diazomethane

Two grams of purified methanol lignin was dissolved in 20 cc. of dioxane and the diazomethane prepared from 10 cc. of nitrosomethyl urethane was passed into the solution at 5° C. The reaction product was allowed to stand for 18 hr. at room temperature and was then heated to 50° C. for 15 min. This brought about the separation of a slimy precipitate which, on centrifuging, floated on the surface of the solution. After filtration, the clear solution was added dropwise to well stirred dry ether. The methylated methanol lignin separated out as a very fine light-brown powder. This was centrifuged, redissolved in dioxane and again precipitated with ether. The product was washed with ether and then twice with petroleum ether. Yield, 1.7 gm. The low yield was due to losses incurred in filtration. The product prior to analysis was dried to constant weight in an Abderhalden oven at 110° C. and 2 mm. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OH)_3$, [900.4]:—C, 65.3; H, 6.2; OCH_3, 24.1%. Found:—C, 66.15, 66.44; H, 6.30, 6.41; OCH_3, 24.9, 24.9, 24.6%.

Methanol lignin methylated with diazomethane shows a degree of solubility in organic solvents similar to that found for the original methanol lignin, but differs however from the latter in that it is insoluble in dilute sodium hydroxide.

In a second experiment the yield of purified product was quantitative and the same methoxyl value was obtained on analysis.

Acetylation of Methanol Lignin Premethylated with Diazomethane

Methanol lignin (2.8 gm.), premethylated with diazomethane, was dissolved in 15 cc. of pyridine and 10 cc. of acetic anhydride added. After standing for 48 hr. at room temperature the mixture was poured on to ice, the precipitated product filtered off, and dried in a vacuum desiccator over sulphuric acid and sodium hydroxide. It was purified by solution in dioxane and precipitation with ether. After it had been washed several times with petroleum ether, the product was dried at 100° C. and 2 mm. pressure for 24 hr. Yield, 3 gm. The acetylated product shows a behavior similar to that of the acetylated methanol lignin with respect to organic solvents. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OCOCH_3)_3$, [1026.5]:—$OCH_3$, 21.1%. Found:—$OCH_3$, 21 4, 21.5%.

Preparation of the Fully Methylated Methanol Lignin by Simultaneous Deacetylation and Methylation

Methanol lignin (2.6 gm.), methylated with diazomethane and then completely acetylated, was dissolved in 30 cc. of acetone and then subjected to a combined deacetylation and methylation treatment at 40° C. with 30 cc. of dimethyl sulphate and 65 cc. of sodium hydroxide solution (30%). The reagents were added in five portions at intervals of 30 min., and the mixture was kept slightly alkaline. The acetone was then distilled off, whereupon the reaction product separated as a sticky mass, which, on cooling, became solid. It was filtered off, ground in a mortar with water in order to remove the sodium sulphate, redissolved in acetone and remethylated, using the same amount of reagents and under the same conditions. The isolated product was purified by dissolving in dioxane and precipitating with dry ether. It separated as a fine light-brown powder, which was centrifuged, washed with ether, then twice with petroleum ether and dried in a desiccator over sulphuric acid. Yield, 2.3 gm. Prior to analysis the product was dried at 110° C./2 mm. Calcd. for $C_{42}H_{32}O_6(OCH_3)_{10}$, [942.7]:—C, 66.2; H, 6.6; OCH_3, 32.9%. Found:—C, 66.36, 66.05; H, 6.64, 6.53; OCH_3, 32.3%.

On repeating the methylation no increase in the methoxyl content was found. Also, treatment of this product with pyridine and acetic anhydride brought about no change in methoxyl value, indicating absence of free hydroxyl groups.

The fully methylated methanol lignin is soluble in acetone, methyl and ethyl alcohols and benzene, insoluble in ether, petroleum ether, water and sodium hydroxide. On heating with dilute sulphuric acid (5%) at 100° C. in aqueous acetone solution, no change in the methoxyl content takes place, indicating the absence of any readily hydrolyzable methoxyl groups.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XIII. THE STRUCTURE AND PROPERTIES OF GLYCOL LIGNIN[1]

By K. R. Gray[2], E. G. King[3], Fritz Brauns[4] and Harold Hibbert[5]

Abstract

Lignin was extracted from spruce wood meal with ethylene glycol containing (*a*) 0.05% and (*b*) 0.2% hydrogen chloride. On purification the two glycol lignins were found to contain 16.9% OCH_3 and 62.8% C., and 16.5% OCH_3 and 64.7% C. respectively. The aqueous glycol mother liquor was found to contain a soluble lignin-carbohydrate compound. The glycol lignin could be separated into a chloroform-insoluble and a chloroform-soluble fraction, each having the same chemical composition and yielding the same methylated products. From the glycol lignin, purified by means of dioxane-ether, acetylated and methylated derivatives were prepared, as were also trityl derivatives of glycol lignin and premethylated glycol lignin

The introduction of three trityl groups indicates the presence of three primary alcohol groups in the original lignin. Glycol lignin can be both partially and completely demethylated by use of hydriodic acid. The effect of the glycol radical on the methoxyl value in the Zeisel determination was studied and an equation derived for the correction of the methoxyl value. The bearing of the results on the formula proposed previously (1) for methanol lignin is discussed.

Introduction

It has been shown in previous communications (3, 4) that lignin can be extracted from wood with ethylene glycol in the presence of small amounts of hydrogen chloride as catalyst. Lignin derivatives isolated in this way were originally thought to be acetals but are now regarded as ethers of the lignin and the alcohol (1).

In order to determine how much lignin can be extracted from the wood in this way, four successive extractions were carried out with ethylene glycol containing 0.05% hydrogen chloride, and the progress of the extraction followed by analysis of the wood meal residues. The percentage of lignin extracted and that isolated after each extraction together with the corresponding results given by Hibbert and Marion are shown in Table I.

The process of preparing glycol lignin involves only slight mechanical losses, so that the large lignin losses (almost 50% in the first and second extractions) (Table I) must have been due to lignin remaining in the aqueous solution when the glycol lignin was precipitated by pouring the glycol solution

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TABLE I

COMPARISON OF AMOUNTS OF LIGNIN EXTRACTED AND ACTUALLY RECOVERED

—	Lignin extracted*		Crude lignin isolated*		Purified lignin isolated*
	Gray	Hibbert and Marion†	Gray	Hibbert and Marion	Gray
In first extraction	46.53	36.7	24.35	20.5	22.0
In second extraction	28.89	12.7	14.6	8.2	13.8
In third extraction	3.06	—	3.3	—	2.95
In fourth extraction	2.38	—	2.2	—	1.9
Total of all extractions	80.86	49.4	44.45	28.7	40.65

**Calculated as percentage of original lignin in wood meal.*

†The figures are calculated from results given by Hibbert and Marion (3) for extractions carried out under conditions identical with those employed by the authors; namely, the use of anhydrous glycol containing 0.05% hydrogen chloride at a temperature of 107–109° C. for eight hours.

into water. This loss may be due either to a solubility effect of the water-glycol mixture, or to the presence of a soluble lignin-carbohydrate complex present in the wood or formed during the extraction.

The possible role played by the "soluble lignin" in the aqueous glycol mother liquor was investigated by studying the effect of concentrating the glycol lignin extract prior to precipitation with water. It was found that the decrease in loss after concentration was only 32.9% of that occurring when the glycol extract was not concentrated.

It was possible to isolate from the aqueous glycol mother liquor a lignin compound in a small yield by precipitating with basic lead acetate. This product appeared to be a compound of lignin with a carbohydrate. After careful decomposition with dilute sulphuric acid, a brown solution was obtained which reduced Fehling's solution only when hydrolyzed with hydrochloric acid, yielding a water-insoluble precipitate with a methoxyl content of 14.2%, but soluble in dioxane and dilute sodium hydroxide solution. The colorless filtrate from the hydrolysis reaction reduced Fehling's solution very strongly. Acetylation of the lead salt gave a product with a large acetyl value and a correspondingly low methoxyl content.

Glycol lignin, purified by adding its dioxane solution to ether, thus precipitating a fine powder, has a methoxyl content of 16.9%, the same value as that found first by Rassow and Gabriel (5), and this value did not change on further purification with other solvents or on hydrolysis. Rassow and Gabriel (5) assumed that their glycol lignin did not contain bound glycol. In order to settle this question, since the presence of glycol may affect the methoxyl determinations, several attempts were made to hydrolyze off the glycol radical and to isolate the glycol, but they were unsuccessful. The proof of the presence of glycol was finally obtained indirectly by using glycol monomethyl ether instead of glycol as extraction medium. The glycol monomethyl ether lignin so obtained had a methoxyl content of 20.5%, *i.e.*, approximately one methoxyl group more on the basis of a molecular weight of about 900.

In order to investigate the influence of the glycol radical on the methoxyl determination, such determinations were carried out on a number of known glycol derivatives of varying molecular weight, as shown in Table II. The methoxyl value did not decrease in exact proportion to the increase in molecular weight. By multiplication of the found methoxyl percentage due to glycol (Table II, Column 3) by the molecular weight of the respective glycol compound, a correction factor for each compound is obtained, and these factors (Column 4) are seen to vary within wide limits from 765 to 1095, the average value being 895.

TABLE II

APPARENT METHOXYL VALUE GIVEN BY A GLYCOL GROUP

Compound	Found OCH_3, %		OCH_3 due to presence of glycol radical, %	Glycol correction factor (% OCH_3 mol. wt.)	OCH_3, %, (K) calcd. from the mean correction factor and the mol. wt. $K = \frac{895}{\text{m.w.}}$
(*a*) Ethylene glycol (m.w. 62)	12.03 12.56	12.30	12.30	765	14.40
(*b*) Glycol dimethyl ether (m.w. 90)	77.21 77.90	77.56	8.67	780	9.90
(*c*) Glycol dicaprate (m.w. 370)	2.39 2.05	2.22	2.22	821	2.42
*(*d*) Tetra-acetyl glycol glucoside (m.w. 392)	1.83 2.03	1.93	1.93	757	2.29
(*e*) Glycol dimyristate (m.w. 482)	2.09 1.90	2.00	2.00	964	1.86
(*f*) Glycol dipalmitate (m.w. 542)	1.74 1.97	1.85	1.85	1003	1.65
(*g*) Glycol distearate (m.w. 595)	1.62 1.66	1.64	1.64	976	1.50
*(*h*) Hepta-acetyl glycol cellobioside (m.w. 680)	1.53 1.69	1.61	1.61	1095	1.22
				Mean 895	

**These two products were prepared for us by Dr. M. L. Wolfrom, The Ohio State University, to whom we wish to express our best thanks for this kindness.*

Applying this value to glycol lignin with a molecular weight of 916, the correction is found to be 0.97%, that is the methoxyl value found would be too high by this amount owing to the glycol in the lignin. In compounds with molecular weights greater than 1800, for example the phenol glycol lignins, the error is within the experimental error.

In any case it is evident that glycol lignin is not very suitable for studies on the structure of lignin when conclusions are to be based on the methoxyl determinations.

The carbon content of the glycol lignin obtained by extracting with 0.05% hydrogen chloride is 62.8%, while that obtained by the use of 0.2% hydrogen chloride is 64.5%, the latter value being also found by Rassow and co-workers. The methoxyl values do not show any difference, and the differences in carbon content disappear in the methylated and acetylated products.

As first shown by Rassow (2, 5, 7) glycol lignin can be separated into a chloroform-insoluble and a chloroform-soluble fraction, amounting to 75 and 25% respectively. The analytical data obtained for the two fractions and their methylated derivatives are shown in Table III and are seen to be in close agreement.

TABLE III

ANALYSIS OF CHLOROFORM FRACTIONATION PRODUCTS AND THEIR DERIVATIVES

Lignin derivative	Chloroform-insoluble fraction, %		Chloroform-soluble fraction, %	
Untreated fraction	(OCH_3) C H	16.95 62.61 6.22	(OCH_3) C H	16.90 63.15 6.43
Methylated with diazomethane	(OCH_3)	21.02	(OCH_3)	21.36
Fully methylated	(OCH_3)	32.00	(OCH_3)	32.2

Using glycol lignin purified twice from dioxane and ether a series of glycol lignin derivatives was prepared. These comprised the acetyl, benzoyl, *p*-brombenzoyl, *p*-nitrobenzoyl and *p*-toluene sulphonyl derivatives. On methylation of glycol lignin with diazomethane a derivative with a higher methoxyl content could be prepared which, as shown both by acetylation and benzoylation, still contained free hydroxyl groups. The complete methylation of glycol lignin was carried out by a simultaneous deacetylation and methylation of two products: (a) the fully acetylated glycol lignin, and (b) the acetylated glycol lignin previously methylated with diazomethane. In both experiments the same fully methylated product was obtained, with a methoxyl content of 31.4% for each product.

On treatment of glycol lignin, as well as of its diazomethane-methylated product, with trityl chloride in pyridine solution, trityl derivatives were obtained. The glycol lignin derivative was found to contain four trityl groups. There seems to be no doubt that one of these has replaced the hydrogen atom in the free hydroxyl of the glycol group, while a second has been substituted for the hydrogen in the phenolic hydroxyl group. The diazomethane-methylated glycol lignin derivative contained only three trityl groups, since in this product the phenolic hydroxyl group has already been methylated by the diazomethane. In both cases there has been left one free hydroxyl group. On acetylation of these products the methoxyl value decreased somewhat, but on account of the high molecular weights in question no conclusions can be drawn from these latter experiments. The introduction of three trityl groups, however, into both the glycol lignin and the premethylated glycol lignin indicates the presence of three primary alcohol groups in the glycol lignin.

In an earlier paper by Brauns and Hibbert (1) a formula for glycol lignin was proposed which was derived from the analysis of the fully methylated, ether-insoluble glycol lignin and independent of that of the fully methylated ether-insoluble methanol lignin. The authors do not wish to be considered as regarding this formula as something definitely and finally proved. As long as there is no other more suitable formula for the glycol lignin unit available, that represented by $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OCH_2CH_2OH)$ will be adopted, and the calculated theoretical data given in the experimental part are based on it.

Attempts were made to demethylate glycol lignin and it was found that partial demethylation could be effected by heating its acetylated product with a mixture of acetic anhydride and glacial acetic acid saturated with hydrogen bromide at 120° C. for two hours. A product with 10.7% OCH_3 (equivalent to four methoxyl groups based on the foregoing formula) is obtained, while complete demethylation can be effected using hydriodic acid and phenol (Zeisel method). The product obtained in the latter case is soluble in dioxane and undoubtedly represents a phenol condensation product of the demethylated phenol lignin. Further investigations in this direction are in progress.

Experimental

Preparation of the Wood Meal

The wood used for the preparation of the lignin was a section of a log* from a freshly cut Northern Ontario white spruce tree about forty years old. The wood was converted to a fine flour by shaving, followed by grinding in a ball mill. The wood flour was screened and those portions passing through 65 and 100 mesh sieves used for the extractions. For analysis it was dried at 110° C./2 mm. over phosphorus pentoxide. Found: OCH_3, 4.88; lignin, 28.94; cellulose, 51.90; acetyl, 1.26; ash, 0.25%.

After it had been dried, the wood meal was extracted for 24 hr. in a Soxhlet extractor with a mixture of equal parts by volume of benzene and 95% alcohol. The wood meal was then dried at 60° C. in a vacuum oven, and extracted with water at 50° C. and again dried at 60° C. in the vacuum oven.

Kindly supplied by the Abitibi Power and Paper Company, Iroquois Falls, Ontario.

Extraction of the Wood Meal with Anhydrous Ethylene Glycol Containing 0.05% Hydrogen Chloride, and Isolation of the Crude Lignin

About 800 gm. of the extracted and well dried wood meal was heated for eight hours at 107–109° C. with 10 times its weight of anhydrous ethylene glycol containing 0 05% of anhydrous hydrogen chloride. The extraction was carried out in a 12 litre flask fitted with a motor-driven stirrer and thermometer, and during the process a stream of dry nitrogen was passed through the apparatus. The mixture was filtered, while hot, in a nitrogen atmosphere. The wood meal residue was washed thoroughly with hot glycol and the filtrate and washings combined. The glycol solution was then added in a fine stream, with stirring, to four times its volume of distilled water previously warmed to 50° C. The precipitated light-brown lignin was allowed to settle, washed four times with distilled water by decantation, filtered, again washed with distilled water and finally dried in a vacuum desiccator over sulphuric acid.

Each lot of the wood meal was extracted four times. After each extraction, the wood meal was washed with distilled water to remove the glycol, dried in the vacuum oven and analyzed.

Purification of the Crude Glycol Lignin

Crude, dry glycol lignin (20 gm.) was dissolved in 100 cc. of pure, warm dioxane. The solution was centrifuged, decanted from a small amount of residue and the latter extracted with another small portion of dioxane The solution was filtered, concentrated to approximately 10% lignin content, and added dropwise to 1200 cc of ether, stirred mechanically. The precipitated lignin was allowed to settle, the ether replaced by fresh ether and the lignin centrifuged. It was washed three times with dry ether, and again centrifuged. After washing in the same manner twice with dry petroleum ether (30–50° C.), it was dried in a vacuum desiccator over sulphuric acid and solid sodium hydroxide. The product so obtained was a buff-colored amorphous powder, the particles of which readily acquired electrostatic charges.

Two lots of purified glycol lignin from two different extractions were analyzed. Found:—Lot I: C, 62 8, 62 8; H, 6 5, 6 6; OCH_3, 16 7, 17 0%. Lot II: C, 62 8, 62 7; H, 6 0, 6 1; OCH_3, 16 8, 17 1, corr.* 15 9, 16 1%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OH)(OH)_4$, [916 5]: C, 64 2; H, 6.2; OCH_3, 16.9%.

The glycol lignin was readily soluble in dioxane, glycol monomethyl ether, methyl and ethyl alcohols (90%), phenol, aqueous acetone, pyridine, and in dilute sodium hydroxide, partly soluble in chloroform and absolute acetone, and insoluble in benzene, ether, petroleum ether and water.

A third and fourth extraction of the same lot of wood meal yielded only a very small amount of glycol lignin with a lower methoxyl content (16 0%; corr. 15 0%).

**Owing to the presence of the glycol radical it is necessary to apply a correction factor (see Table II) to the experimental methoxyl values obtained.*

Extraction of the Wood Meal with Glycol and 0.2% Hydrogen Chloride, and Isolation of the Crude Lignin

The extraction was carried out in the same manner but using 518 gm. of wood meal and five litres of ethylene glycol containing 0.2% hydrogen chloride.

The filtered glycol solution was divided into two equal parts. One was precipitated without further treatment, as described above, while the other was concentrated to one-quarter the volume. The non-concentrated solution yielded 30.0 gm. of crude, dry glycol lignin and the concentrated solution gave 34.1 gm.

The total residual wood meal from this experiment was washed once with glycol and was then washed thoroughly with four litres of methyl alcohol. The dissolved glycol lignin was isolated by concentrating under diminished pressure and adding the filtered solution dropwise to four times its volume of distilled water. Yield, 10.2 gm. The total yield of crude lignin was 74.4 gm. or 51.7% of the lignin contained in the original spruce wood meal.

The crude glycol lignin (64 gm.) obtained from both precipitations was purified by the method described above. Yield, 56 gm. Found: C, 64.6, 64.9; H, 6.0, 5.8%. Methoxyl determinations: After one precipitation from dioxane:—OCH_3, 16.6, 16.5%; corr., 15.6, 15.5%; after a second precipitation from dioxane:—OCH_3, 16.5%; corr., 15.5%; after precipitation from acetone:—OCH_3, 16.5, 16.4%; corr., 15.5, 15.4%. The product was, therefore, considered to be homogeneous with regard to methoxyl content. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OH)(OH)_4$, [916.5], C, 64.2; H, 6.1; OCH_3, 16.9%.

Extraction of Wood Meal with Ethylene Glycol Monomethyl Ether Containing 0.1% Hydrogen Chloride

The procedure was the same as that employed in the extraction of the wood meal with ethylene glycol.

From 241 gm. of dry wood meal (65 mesh) there was obtained 14.5 gm. crude, dry glycol monomethyl ether lignin, or 6.0% of the weight of the original wood meal.

The product was almost completely soluble in dioxane and was purified by adding the dioxane solution to ether, thus precipitating the product, using exactly the same technique as for glycol lignin. The purified product was a fawn-colored powder. Yield, 12.2 gm.

The product was soluble in dioxane, glycol monomethyl ether, alcohol (95%), chloroform, and insoluble in benzene, ether, water, sodium carbonate solution, etc. Found: OCH_3, 20.5%; corr. 19.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OCH_3)(OH)_4$, [930.5]: OCH_3, 20.0%.

Acetylation of Glycol Lignin

Two grams of glycol lignin was dissolved in 10 cc. of dry pyridine and 5 cc. of acetic anhydride added. After it had stood for 24 hr. at room temperature, the clear solution was poured into ice water. The light-brownish precipitate separating out was filtered, washed with distilled water, and dried over sulphuric acid and sodium hydroxide in a vacuum desiccator. It was purified by dissolving it in dry chloroform and pouring the solution, drop by drop, into absolute methyl alcohol, with vigorous stirring. The isolated product was redissolved in dioxane and precipitated again with ether. Yield, 2.2 gm. For the analysis it was dried in an Abderhalden over phosphorus pentoxide at 78° C./2 mm. Found: C, 62.16, 62.20, 62.37; H, 5.67, 5.68, 5.81; OCH_3, 14.1%; corr. 13.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OOCCH_3)(OCOCH_3)_4$, [1126.5]: C, 62.9; H, 5.9; OCH_3, 13.8%. The acetylated glycol lignin is soluble in dioxane, chloroform, pyridine, glacial acetic acid and acetone; it is insoluble in methyl alcohol, ether, water and cold dilute sodium hydroxide solution.

Benzoylation of Glycol Lignin

Two grams of glycol lignin was dissolved in 15 cc. of dry quinoline and 6 cc. of benzoyl chloride added. After about one hour, crystallization of quinoline hydrochloride began and the product was allowed to stand at room temperature for 24 hr. The mixture was then poured into ice-cold sulphuric acid (5%), whereupon a sticky mass separated out. It was kneaded with water but did not become solid. The sticky, dark brown product was dissolved in chloroform, this solution washed with water, dilute sulphuric acid, 5% potassium bicarbonate solution and finally with water. It was then dried with calcium chloride and the benzoylated lignin precipitated by pouring the solution into dry methyl alcohol. It separated out as a fine, light-red powder which was dried over calcium chloride and phosphorus pentoxide. Yield, 2.8 gm. It was purified further by adding its dioxane solution dropwise to dry ether. For the analysis the product was dried at 100° C./2 mm. Found: C, 70.65, 70.75; H, 5.22, 5.08; OCH_3, 11.4; corr. 10.8%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OOCC_6H_5)(OOCC_6H_5)_4$, [1436.6]: C, 70.1; H, 5.3; OCH_3, 10.8%. The benzoylated glycol lignin is soluble in chloroform, dioxane, pyridine and quinoline, but insoluble in ether, petroleum ether, methyl alcohol and water.

Preparation of p-Brombenzoyl Glycol Lignin

Two grams of glycol lignin was dissolved in 10 cc. of dry pyridine and a solution of 5 gm. of *p*-brombenzoyl bromide added. The mixture became hot and was cooled with ice water. It was then allowed to stand at room temperature for 24 hr., poured into ice water and the solid precipitate filtered off. After it had been dried in a desiccator over sodium hydroxide and sulphuric acid, it was purified by dissolving it in chloroform and adding the solution dropwise to well stirred dry ether. Yield, 2.2 gm. Further purification was effected by adding its dioxane solution dropwise to dry ether. Found: Br, 25.6; OCH_3, 7.1; corr. 6.7%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OOCC_6H_4Br)(OOCC_6H_4Br)_4$, [1831.2]: Br, 21.5; OCH_3, 8.5%. Calcd. for* $C_{42}H_{32}O_6(OCH_3)_4(OCH_2CH_2OOCC_6H_4Br)(OOCC_6H_4Br)_5$, [2001.2]:

**In the case that one methoxyl group is split off and replaced by a p-brombenzoyl group.*

Br, 24.0; OCH_3, 6.3%. The *p*-brombenzoyl glycol lignin is soluble in chloroform, dioxane, and acetone, but insoluble in ether, petroleum ether, methyl alcohol and water.

Preparation of p-Nitrobenzoyl Glycol Lignin

Two grams of glycol lignin was dissolved in 12 cc. of dry pyridine and mixed with a solution of 5 gm. of nitrobenzoyl chloride in 5 cc. of dry chloroform. After it had stood for 48 hr. at room temperature, the product was isolated in the same manner as in the case of the benzoyl glycol lignin. Yield, 2.2 gm. Found: OCH_3, 8.6%, corr. 8.1%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OOCC_6H_4NO_2)(OOCC_6H_4NO_2)_4$, [1661.5]: OCH_3, 9.3%. The solubility relations of this compound are the same as those of benzoyl glycol lignin.

Preparation of Glycol Lignin p-Toluene Sulphonate

Two grams of glycol lignin was dissolved in 15 cc. of dry pyridine and 5 gm. of *p*-toluene sulphonyl chloride added. After a short time crystallization of pyridine hydrochloride began. The mixture was allowed to stand for 24 hr. at room temperature, then poured on to ice water, the ester separating as a very fine light-brown precipitate. This was filtered and dried in a vacuum desiccator over sulphuric acid and solid sodium hydroxide. The crude product was dissolved in dry chloroform and reprecipitated as in the case of acetyl lignin. It was purified by redissolving it in chloroform and adding the solution dropwise to ether. Yield, 3 1 gm. For the analysis the product was dried in an Abderhalden at 100° C./2 mm. Found: OCH_3, 8.5%, corr. 8.0%; S, 9 7, 9 65%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OSO_2C_6H_4CH_3)(OSO_2C_6H_4CH_3)_4$, [1687 1]: OCH_3, 9.2; S, 9 5%. The glycol lignin toluene sulphonate is soluble in pyridine, chloroform and dioxane, but insoluble in ether, benzene, petroleum ether, water and dilute alkali solution.

Methylation of Glycol Lignin with Diazomethane

Two grams of purified glycol lignin was dissolved in 15 cc. of dry dioxane and a solution of diazomethane (prepared from 10 cc. of nitrosomethyl urethane) in 10 cc. of dry dioxane added at room temperature. A slow evolution of nitrogen occurred and the solution became lighter in color. The mixture was allowed to stand overnight at 15° C. The next day a similar quantity of the diazomethane solution was added and the mixture allowed to stand for another 24 hr. at room temperature. A small, slimy precipitate separated out. This was coagulated by heating the solution to 50° C. for 15 min.; the mixture was then centrifuged, filtered and the clear solution concentrated under reduced pressure. The methylated glycol lignin was isolated by pouring the solution into dry ether with vigorous stirring. The precipitated product was washed with dry ether and finally twice with petroleum ether. The diazomethane-methylated glycol lignin so obtained was a very finely divided, light-brown powder. Yield, 2.1 gm. Found: C, 63.90, 64.04; H, 6.31, 6.38; OCH_3, 21.2, 21.0%, corr. 20.2, 20.0%.

Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OH)(OH)_3$, [930.5]: C, 64.4; H. 6.3; OCH_3, 20.0%. The methylated glycol lignin thus obtained is soluble in dioxane, pyridine, acetone, chloroform, methyl and ethyl alcohols, but insoluble in ether, petroleum ether, water and sodium hydroxide. A further methylation with diazomethane did not increase the methoxyl content. Found: OCH_3, 21.0%, corr. 20.0%.

Acetylation of Glycol Lignin Premethylated with Diazomethane

Two grams of glycol lignin, premethylated with diazomethane, was acetylated under the same conditions as those described for glycol lignin. The product, after precipitation from water, was dried over sodium hydroxide and sulphuric acid, and purified by precipitating twice from dioxane and ether (light yellowish powder, yield quantitative). Found: C, 63.50, 63.50; H, 6.18, 6.00; OCH_3, 17.5, 17.3%, corr. 16.7, 16.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OOCCH_3)(OOCCH_3)_3$, [1098.5]: C, 63.3; H, 6.0; OCH_3, 16.9%. The acetyl derivative of the glycol lignin premethylated with diazomethane is soluble in acetone, dioxane, chloroform, but insoluble in ether, petroleum ether, water and dilute sodium hydroxide.

Benzoylation of Glycol Lignin Premethylated with Diazomethane

Two grams of glycol lignin premethylated with diazomethane was benzoylated using dry quinoline and benzoyl chloride, following the method used for glycol lignin. Yield, 2.5 gm. For the analysis it was dried at 100° C./2 mm. Found: C, 69.42, 69.58; H, 5.41, 5.41; OCH_3, 13.8, 13.6, corr. 13.1, 12.9%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OOCC_6H_5)(OOCC_6H_5)_3$, [1346.6]: C, 69.5; H, 5.5; OCH_3, 13.8%. Its solubility relations are similar to those of the benzoylated glycol lignin.

Preparation of the p-Toluene Sulphonyl Ester of the Glycol Lignin Premethylated with Diazomethane

This compound was prepared in the manner described for the corresponding compound of glycol lignin. Yield from 1 gm. of premethylated glycol lignin, 1.7 gm. Found: OCH_3, 11.9, corr. 11.3%; S, 7.7, 7.83%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OSO_2C_6H_4CH_3)(OSO_2C_6H_4CH_3)_3$, [1546.9]: OCH_3, 12.0; S, 8.2%.

Complete Methylation of Glycol Lignin

This experiment was carried out in two different ways. In the first method the glycol lignin, premethylated with diazomethane, was used, but in the second, the acetylated glycol lignin was methylated by a simultaneous deacetylation-methylation process.

(a) Methylation of Glycol Lignin Premethylated with Diazomethane

Seven grams of premethylated lignin was acetylated as described previously and the acetylated product dissolved in 100 cc. of acetone. A simultaneous deacetylation and methylation was then carried out with 85 cc. of dimethyl sulphate and 175 cc. of 30% sodium hydroxide solution. The reagents were added drop by drop in ten portions at intervals of 10–15 min. The temperature was maintained at 56° C. and the solution kept slightly alkaline throughout the process. After the last addition, the reaction mixture was stirred for a further two hours at the same temperature. The product then consisted of two layers which formed an emulsion on stirring. The acetone was distilled off, whereupon the mass separated out on the surface of the aqueous solution as a sticky mass, which solidified on cooling. It was filtered, washed with water and dried in a desiccator over sulphuric acid. This product was remethylated under the same conditions and the isolated product, after it had been dried in a desiccator, was extracted with acetone in a Soxhlet apparatus. The acetone solution was centrifuged, filtered and the product precipitated by pouring the solution into dry ether. A third methylation was then carried out under the same conditions and the product isolated as before. After purification by solution in acetone and precipitation with ether, the product was washed several times with petroleum ether. A sample was dried at 78° C./2 mm. Found: OCH_3, 31.4%. This product was remethylated a fourth time in the same manner and purified. Yield, 5.5 gm. Found: C, 65.83, 65.41; H, 6.76, 6.86; OCH_3, 31.3, corr. 30.4%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OCH_2CH_2OCH_3)$, [986.5]: C, 65.7; H, 6.7; OCH_3, 31.4%.

In order to find out whether this product was completely methylated, 0.5 gm. was submitted to an acetylation treatment with pyridine and acetic anhydride. A methoxyl determination of the isolated and purified product gave 31.57%. Since no decrease in the methoxyl content occurred, it is obvious that the product had been completely methylated. The fully methylated glycol lignin is soluble in acetone, pyridine, and dioxane, but insoluble in ether, petroleum ether, water and dilute sodium hydroxide solution.

(b) Methylation of Acetylated Glycol Lignin

Acetylated glycol lignin (6 gm.) was dissolved in 80 cc. of acetone and a combined deacetylation-methylation carried out with dimethyl sulphate and sodium hydroxide solution. Dimethyl sulphate (80 cc.) and sodium hydroxide (30%; 180 cc.) were added in five portions at intervals of 30 min. After the last addition, the reaction mixture was stirred for another hour. The methylated glycol lignin was isolated and purified as described under (*a*). After two methylations a sample was isolated, purified and dried at 78° C./2 mm. Found: OCH_3, 31.9%. This product was remethylated under the same conditions, isolated and purified. Yield, about 75%. Found: C, 65.11, 65.53; H, 6.65, 6.76; OCH_3, 31.4, corr. 30.4%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OCH_2CH_2OCH_3)$, [986.5]: C, 65.7; H, 6.7; OCH_3, 31.4%. These analytical data agree very well with those of the former experiment.

As indicated by the low yield and the color of the dioxane-ether solution, an appreciable amount of the lignin product must have remained dissolved in the mother liquor. This was isolated by completely evaporating the solvents, dissolving the light-brown viscous syrup in dry benzene and precipitating the product by adding the clear solution to well stirred petroleum ether. An orange-yellow powder separated. This was washed with fresh petroleum ether, filtered and dried over sulphuric acid. Found: OCH_3, 32.7%.

In the same way the product from the diazomethane-ether mother liquor of Experiment (*b*) was isolated in a yield of 22%. Found: OCH_3, 35.0%.

Preparation of a Trityl Derivative of Glycol Lignin

Glycol lignin (2.5 gm.) was dissolved in 15 cc. of dry pyridine and 2.5 gm. of trityl chloride added to the solution. The trityl chloride dissolved rapidly without any appreciable generation of heat. The mixture was heated to about 70° C. in a water bath for 15 min. and then allowed to stand for 48 hr. at room temperature. It was poured on to cracked ice, the precipitate filtered, washed with water and dried in a desiccator over sulphuric acid. The product was then dissolved in dioxane and the solution added, drop by drop, to dry ether, with vigorous stirring. The fine, powdery product was centrifuged, washed with fresh ether, again dissolved in dioxane and reprecipitated with ether. After centrifuging, washing with ether and petroleum ether, the product was dried at 100° C./2 mm. Yield, 4 gm. Found: OCH_3, 8 4, 8.6; corr. 8.0, 8.2%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OC(C_6H_5)_3)(OC(C_6H_5)_3)_3(OH)$, [1888.5]: OCH_3, 8.2%.

Acetylation of the Previous Product

Trityl glycol lignin (2 gm.) was acetylated with pyridine and acetic anhydride and worked up as usual. Yield, 22 gm. It was purified by dissolving it in dioxane and pouring the solution into dry ether. The fine light-brown powder that was precipitated was centrifuged and washed with ether and petroleum ether. Found: OCH_3, 8.3, 8.3; corr., 7.9, 7.9%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCH_2CH_2OC(C_6H_5)_3)(OC(C_6H_5)_3)_3(OCOCH_3)$, [1930.5): OCH_3, 8.0%.

Preparation of the Trityl Derivative of Glycol Lignin Premethylated with Diazomethane

Glycol lignin (1 gm.), premethylated with diazomethane, was treated with trityl chloride (2 gm.) in pyridine solution and worked up in the same way as that described for the original glycol lignin. Yield, 1.9 gm. Found: OCH_3, 11.4, 11.2%; corr., 10.9, 10.7%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OC(C_6H_5)_3)(OC(C_6H_5)_3)_2(OH)$, [1659.4]: OCH_3, 11.2%.

Acetylation of the Previous Product

A portion (0.5 gm.) of the product obtained in the previous experiment was acetylated with pyridine and worked up in the usual manner. Found: OCH_3, 10.6, 10.6; corr., 10.2, 10.2%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OC(C_6H_5)_3)(OC(C_6H_5)_3)_2(OCOCH_3)$, [1701.4]: OCH_3, 10.9%.

Attempted Demethylation of Glycol Lignin with Hydrobromic Acid

Acetylated diazomethane-premethylated glycol lignin (0.5 gm.; OCH_3, 17%) was dissolved in a mixture of 5 cc. of acetic anhydride and 5 cc. of glacial acetic acid saturated with hydrobromic acid. The solution was heated in a sealed tube for two hours at 120° C. then poured on to ice, the dark brown precipitate filtered, washed with water and dried over sodium hydroxide and phosphorus pentoxide. For the analysis the product was dried in an Abderhalden at 78° C./2 mm. Found: OCH_3, 10.7%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_4(OCOCH_3)_5(OCH_2CH_2OCOCH_3)$, [1154.5]: OCH_3, 10.7%. The product was free from bromine.

Numerous other experiments were carried out, but with little success.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XIV. THE ACTION OF LEAD TETRA-ACETATE AND OF MERCURIC ACETATE ON GLYCOL LIGNIN DERIVATIVES[1]

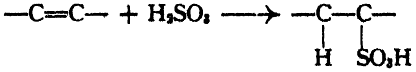
(PRELIMINARY COMMUNICATION)

BY K. R. GRAY[2], FRITZ BRAUNS[3] AND HAROLD HIBBERT[4]

Abstract

Fully methylated glycol lignin (OCH_3, 30.4%) was treated with lead tetra-acetate and with mercuric acetate. In the first case the acetoxyl group was introduced to the extent of 11.5%. With mercuric acetate in alcohol, the sole reaction was the substitution of hydrogen by the $—HgOCOCH_3$ group, there being no addition of ethoxyl nor loss of methoxyl groups. After repeated mercurization the final product contained 42.7% of mercury, that is, a ratio of introduced mercury atoms to original methoxyl groups of 1:1.

The presence of ethylenic bonds in lignin has not been definitely established. To account for the formation of a stable lignin sulphonic acid Klason (22, 23, 24) assumed that a double bond is present and that addition takes place to it as follows:



$$—C{=}C— + H_2SO_3 \longrightarrow —\underset{H}{C}—\underset{SO_3H}{C}—$$

If the addition took place to a carbonyl group there would result an unstable sulphonic acid (21) from which sulphurous acid could be split off readily. Actually it is found that the greater part of the sulphur is firmly bound, apparently in the form of a stable sulphonic acid. The formation of a sulphonic acid does not definitely prove the presence of an ethylene bond, for there are other possibilities such as the sulphonation of a benzene nucleus (25), or the addition to a double bond formed during the reaction by the splitting off of water (10, p. 128).

The fact that gaseous chlorine, in the absence of moisture, has no appreciable action on wood, or on lignin, even at 80° C. is fairly good evidence of the absence of double bonds. On the other hand, Baur (2, 3, 4) has shown that many unsaturated compounds in which the double bonds are conjugated with benzene nuclei do not add halogen or only very slowly.

Many of the workers (5, 17, 19) who have obtained halogen derivatives of lignin have used aqueous or moist gaseous halogens, that is, they have employed conditions which favor oxidation and substitution rather than addition. Other workers (14, 15) have used solutions of dry halogens in non-aqueous solvents, but in nearly all cases have not distinguished between

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substitution and addition. Thus the results of the halogenation experiments are, in general, meaningless as regards the determination of ethylenic linkages in lignin.

A similar uncertainty exists regarding the question whether or not the nucleus of the lignin molecule is of an aromatic nature. It has been established that small amounts of aromatic compounds are formed on fusion with alkali, or on dry distillation, but this is not a certain proof of the presence of an aromatic nucleus since, in reactions of this kind, hydro-aromatic or even aliphatic compounds could easily be converted to aromatic derivatives by oxidation and loss of water. Moreover, since the amount of aromatic constituents isolated is usually small (less than 10%), these reactions convey relatively little enlightenment regarding the nature of the greater part of the lignin molecule.

Brauns and Hibbert (6, 7) have shown that native lignin with a "building unit" having a molecular weight of about 872 contains five hydroxyl groups, one of which can be methylated with diazomethane. This is supporting evidence for the presence of a phenolic hydroxyl group, although the reaction could also be given by an enolic hydroxyl group, as well as certain other derivatives, for example kojic acid (1) and ascorbic acid (18).

The usual methods for the determination of the structure of aromatic compounds have failed when applied to lignin. With halogenation, the results are complicated by partial loss of methoxyl groups (11, 13) and, if moisture is present, also by oxidation changes. Lignin is readily nitrated but simple derivatives are not obtained, owing to the fact that lignin is so readily oxidized and also because the introduced nitrogen is in the form of ester nitrogen (NO_3), nitrosonitrogen (NO), as well as in the form of nitro (NO_2) groups (20).

Since the classical structural methods have, over a long period of years, yielded only questionable information regarding the unsaturation, both ethylenic and aromatic, it would appear that further enlightenment must come through the application of new reagents.

The use of lead tetra-acetate as a reagent for the determination of unsaturated linkages in lignin was first investigated by Freudenberg and coworkers (11). They obtained from "Freudenberg lignin" a derivative with an acetyl content of 5.7%, corresponding to the addition of 7.8% acetoxyl, or to one ethylenic linkage per eight methoxyl groups. Freudenberg (10, p. 127) has, however, suggested that double bonds may not actually exist in lignin, but that they may be formed by splitting off water, prior to addition taking place.

In the present investigation the action of lead tetra-acetate on glycol lignin was investigated and, in order to eliminate the possibility of the formation of double bonds, completely methylated glycol lignin (OCH_3, 31.35%; corrected for glycol, 30.4%) was used. After heating the latter in dioxane solution for five hours with lead tetra-acetate the isolated product had an acetyl content of 7.45%, a methoxyl content of 24.85% (uncorrected), and it contained lead also. The lead was removed by allowing the product to stand in a mixture of acetic anhydride and pyridine for one day. After purification, analyses showed an acetyl content of 8.35%, and a methoxyl content of 26.7%, uncorrected, or 25.9%, corrected for the effect of glycol.

Since the reaction was not repeated owing to lack of material, it cannot be decided whether the reaction was complete. Therefore no conclusions can be drawn regarding the ratio of acetoxyl introduced to methoxyl content.

However, since lead tetra-acetate is capable of replacing labile hydrogen atoms by acetoxyl groups (9), and very little is known regarding the structure of the lignin molecule and the presence or absence of such labile atoms, no definite conclusion at the moment can be reached in this matter.

Mercuric acetate, employed according to the method of Dimroth (8, 9), is one of the best reagents for indicating the presence of an aromatic ring structure. Under its influence the mercuri-acetoxyl ($—HgOOCH_3$) group is introduced into the ring.

Freudenberg (11) was the first to use this reagent in connection with lignin investigations. Treatment of a partially methylated Freudenberg lignin (OCH_3, 28%) yielded a product containing 33% of mercury. The original material, as well as the derivative so obtained, was insoluble in all solvents. The latter substance had a methoxyl value of 13 8% as compared with a theoretical value of 16 0% calculated on the assumption that the only reaction taking place was the replacement of hydrogen in the nucleus by the mercuri-acetoxyl radical.

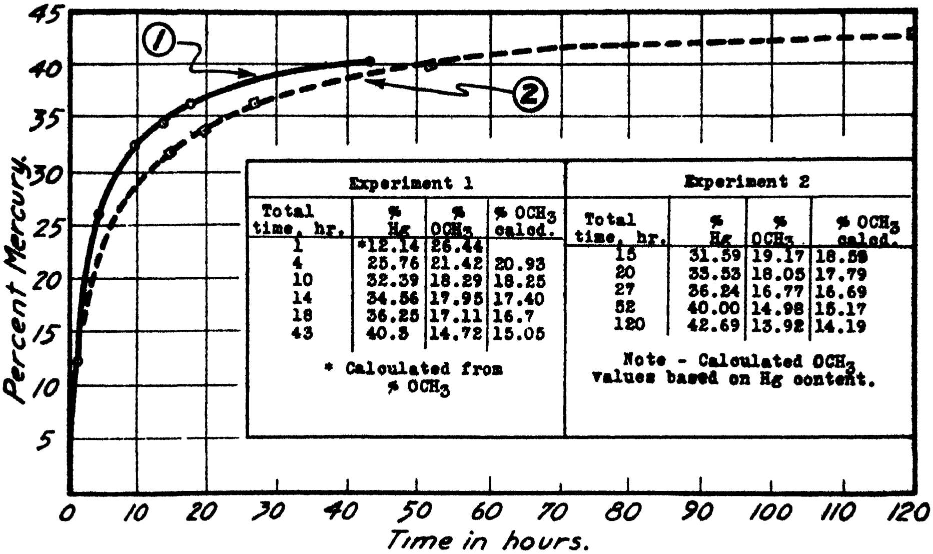
In the present investigation conditions were more favorable inasmuch as both the original lignin product and its reaction product were soluble in organic solvents, thus enabling the reaction to be carried out in a homogeneous solution. Under these conditions the completely methylated glycol lignin (OCH_3, 31 35%; corrected for glycol, 30 4%) yields a mercuri-acetoxyl derivative, in which the methoxyl contents throughout the course of the reaction are seen (Fig. 1) to be in close agreement with the theoretical values based on the assumption that the sole reaction is the substitution of hydrogen by mercuri-acetoxyl groups.

Despite the fact that the reaction was carried out in homogeneous solution, the rate was much slower than that found by Freudenberg. This may be due to the fact that Freudenberg used an incompletely methylated lignin. In Fig. 1 curves are shown for two mercurization experiments. In Experiment 1 the mercuric acetate was renewed frequently during the initial period when the rate of reaction was greatest. In Experiment 2 the mercuric acetate was not renewed during the first 15 hr., with the result that the reaction took place more slowly.

Repeated mercurization yields a product with a final mercury content of 42.7% and a corrected methoxyl content* of 13.52%. (The actual OCH_3 value was 13.92%.) On the basis of a molecular weight of 986.5 (6, 16) for fully methylated glycol lignin, the introduction of five mercuri-acetoxyl groups would require a mercury content of 43 8% and a methoxyl value of 13.6%.

**Corrected for the influence of glycol on the methoxyl determination (16).*

The presence of aromatic rings, or of heterocyclic ring derivatives capable of functioning in an analogous manner, is thus indicated. If the reaction is due to the presence of benzene rings, five of these would be indicated, since, with aromatic compounds containing no free hydroxyl groups, the general action of mercuric acetate in alcohol is to introduce only one atom of mercury into an individual ring.



Experiment 1				Experiment 2			
Total time, hr.	% Hg	% OCH_3	% OCH_3 calcd.	Total time, hr.	% Hg	% OCH_3	% OCH_3 calcd.
1	*12.14	26.44		15	31.59	19.17	18.59
4	25.76	21.42	20.93	20	33.53	18.05	17.79
10	32.39	18.29	18.25	27	36.24	16.77	16.69
14	34.56	17.95	17.40	52	40.00	14.98	15.17
18	36.25	17.11	16.7	120	42.69	13.92	14.19
43	40.5	14.72	15.05				

* Calculated from % OCH_3

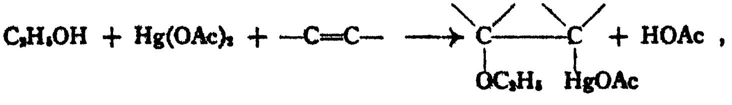
Note - Calculated OCH_3 values based on Hg content.

FIG 1. *Mercurization of fully methylated glycol lignin (the mercuric acetate was renewed after each analysis)*

In the case of furane rings such a generalization cannot be made. The mercurization of these compounds has not been studied as closely as with aromatic compounds, but the available data show that the number of mercury atoms that can be introduced varies markedly with the nature of the substituent.

Since a molecular weight of 916 for the original glycol lignin corresponds to a unit containing five methoxyl groups, the ratio of the number of mercury atoms introduced to the number of original methoxyl groups is nearly 1 : 1, independently of the size of the formula adopted. Freudenberg found only 0 8 atoms of mercury per original methoxyl group (12).

The results of the mercurization experiments also indicate the absence of reactive ethylenic linkages. With an ethylenic linkage the typical reaction of mercuric acetate in absolute ethyl alcohol is the addition of an ethoxyl and a mercuri-acetoxyl group (8, 9).



$$C_2H_5OH + Hg(OAc)_2 + -C{=}C- \longrightarrow \underset{OC_2H_5}{\overset{\diagdown\ \diagup}{C}}-\underset{HgOAc}{\overset{\diagdown\ \diagup}{C}} + HOAc\ ,$$

while actually, in the mercurization of methylated glycol lignin, all the methoxyl values found are in close agreement with the assumption that no ethoxyl has been introduced, the only reaction taking place representing a substitution of nuclear hydrogen by —HgOAc groups.

This is the first known case of a substitution reaction for lignin not involving loss of methoxyl. The reaction would appear to be valuable for structural purposes for the following reasons: (*a*) there is no loss of methoxyl groups; (*b*) the product formed is soluble in organic solvents; (*c*) the number of atoms of mercury introduced bears a simple stoichiometrical relation to the number of methoxyl groups present.

It would seem that very definite and reliable structural information should be yielded by (i) an investigation of the reactions of the fully mercurized product, and (ii) a study of the mercurization of compounds the known structures of which are thought to be similar to that of lignin.

Experimental

Treatment of Fully Methylated Glycol Lignin with Lead Tetra-acetate.

Fully methylated glycol lignin (0 5 gm.; OCH_3, 31 35%; corrected, 30 4%) was dissolved in 5 cc. of dry dioxane, and mixed with 1 8 gm. of lead tetra-acetate dissolved in 20 cc. of the same solvent. The mixture, protected from moisture, was heated at 50° C. for five hours. After cooling, and centrifuging, the small residue, apparently a mixture of lead acetate and lead dioxide was extracted with dioxane. The combined solutions were poured into 300 cc. of ice-water containing 30 cc. of glacial acetic acid, and the precipitated product centrifuged, washed in the centrifuge tube twice with 10% acetic acid, then three times with distilled water and dried. Yield, 0 65 gm.

The crude, dry product was dissolved in 5 cc. of dry benzene, the solution (about 7 cc.) filtered and added dropwise to 70 cc. of well stirred dry ether. The precipitate was centrifuged, washed in the centrifuge tube three times with ether, twice with petroleum ether (b.p. 30–50° C.), and dried, yielding a buff-colored powder having a somewhat more brownish tint than the original material. Yield, 0 50 gm. Found: Acetyl, 7.45%. (Acetoxyl, 10.20%.) The product contained lead.

In order to remove this, the substance was dissolved in a mixture of pyridine and acetic anhydride, and after the solution had stood for 24 hr at room temperature it was poured on to cracked ice, dried and purified as before. The ash content was then only 0 20%.

Analysis (corrected for ash-free product):— Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OCH_2CH_2OCH_3)(OCOCH_3)_2$ [1104.5]: OCH_3, 28.0%; CH_3CO, 7.8%; $(OCOCH_3)$, 10.7%. Found:— OCH_3, 26.7, 26.7; corr. 25.9; CH_3CO, 8.3; $OCOCH_3$, 11.4%.

The Mercurization of Fully Methylated Glycol Lignin

Two lots of fully methylated glycol lignin (OCH_3, 31.35%; corrected, 30.4%) were subjected to repeated mercurization, following the procedure and purification described for the first mercurization. The methoxyl and mercury values obtained after each treatment are given in the Table in Fig. 1.

Methylated glycol lignin (1.0 gm.) was dissolved in a warm mixture of 10 cc. of absolute alcohol and 1 cc. of dioxane. Mercuric acetate (3 gm.) (Kahlbaum) was dissolved in a mixture of 30 cc. of absolute alcohol and 1.5 cc. of glacial acetic acid (the latter being added to prevent hydrolysis), the hot solution filtered and added to the solution of the methylated lignin. The mixture was refluxed on a water bath for 60 min. On cooling, some lignin material separated out. This was redissolved by adding about 5 cc. of dioxane; the solution was filtered to remove a small amount of inorganic salt, and the clear solution then added dropwise to 350 cc. of 2% acetic acid stirred mechanically. The precipitated mercurized methylated lignin was separated by centrifuging, washed five times by stirring with 1% acetic acid and then centrifuged. The last two washings on testing showed no trace of mercury. The mercurized product was dried to constant weight in a vacuum desiccator over sulphuric acid and sodium hydroxide. It was a fawn-colored powder. Yield, 1.35 gm.

The crude, dry product was purified by dissolving in 7 cc. of dioxane, filtering through a small Black Ribbon filter (Schleicher and Schüll), and the combined solution and washings (10 cc.) were added dropwise to 100 cc. of ether stirred mechanically. The precipitate was washed three times by stirring with ether, and centrifuging, and then twice in a similar way using petroleum ether (30–50° C.). The precipitate was allowed to stand overnight in the petroleum ether used for the final washing. The product was dried in a vacuum desiccator over sulphuric acid and sodium hydroxide. It was a fawn-colored powder. Yield, 1.1 gm. Analysis of the final product:– Calcd. for $C_{42}H_{27}O_6(OCH_3)_9(OCH_2CH_2OCH_3)(HgOCOCH_3)_5$(2279.6): OCH_3, 13.9%; Hg, 43.8%; CH_3CO, 9.4%. Found: OCH_3, 13.9, 14.0% (corrected, 13.5, 13.6%); Hg, 42.7%; CH_3CO, 8.4%.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XV. PHENOL GLYCOL LIGNIN[1]

By Fritz Brauns[2] and Harold Hibbert[3]

Abstract

Phenol condensation products of glycol lignin, of a premethylated and a fully methylated glycol lignin have been prepared. In each case it has been found that, on the basis of the five methoxyl groups present in the original glycol lignin, three molecules of phenol react with one lignin unit by nuclear condensation, and when the product is worked up immediately no loss of methoxyl groups occurs. With the fully methylated glycol lignin in one experiment, some of the methoxyl groups were removed but the hydroxyl groups thus formed could not be remethylated with diazomethane, thus indicating their probable aliphatic character. Quercetin does not give a phenol condensation product under the same conditions.

Introduction

As shown in the following paper (2) lignin can be extracted from wood meal by heating with phenol at a low temperature in the presence of dry hydrogen chloride as catalyst, yielding the so-called "phenol lignin". The structure of this compound and the mechanism of its formation are still unknown, in spite of the number of recent investigations (4, 6) carried out on the subject. It was pointed out previously (1) that in this reaction one phenol molecule reacts with the lignin to form a compound having an ether linkage, and three other phenol molecules react stoichiometrically with a lignin unit containing five methoxyl groups. Additional proof of this is now provided in the experimental results described in this paper. When glycol lignin is heated with phenol in the presence of a trace of hydrochloric acid, the color of the phenol lignin solution changes immediately from a reddish- to a violet-brown. The isolated and purified phenol glycol lignin (Formula I) has a methoxyl content of 13 1%, that of the original product being 16.9%. This decrease corresponds exactly with the entrance of three phenol groups into a lignin molecule having the structure $C_{42}H_{32}O_6(OCH_3)_5(OH)_4.(OCH_2CH_2OH).3C_6H_5OH$. In glycol lignin the hydroxyl group capable of etherification by means of alcohol and hydrochloric acid has been replaced by a glycol group, and the three phenol molecules must therefore have all undergone nuclear condensation, thus introducing three new free phenolic hydroxyl groups. This is shown by the methylation experiments with diazomethane, as well as by the results obtained on benzoylation. Methylation with diazomethane indicates that, in addition to the probable presence of one phenolic hydroxyl group in the original glycol lignin, there are present three new phenolic hydroxyl groups originating from the three newly entering phenol molecules.

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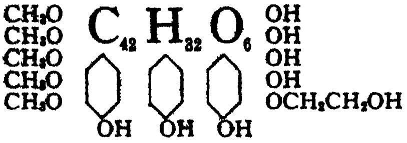

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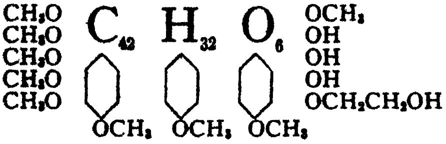

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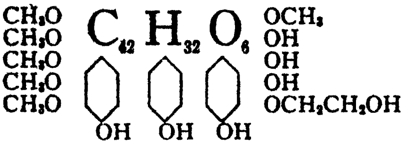

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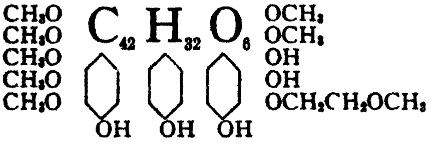

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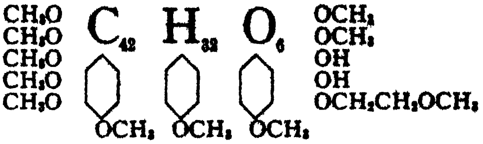

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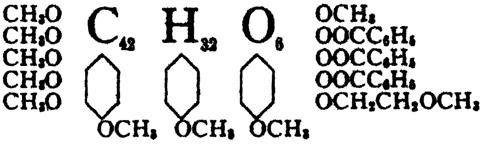

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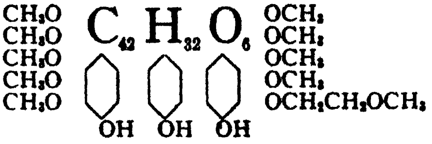

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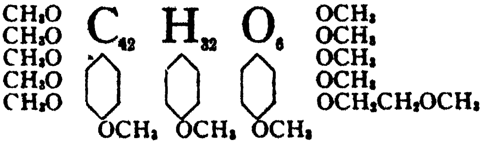

VIII

The presence of other free non-phenolic hydroxyl groups is indicated by the formation of an acetyl derivative on acetylation of the diazomethane-methylated product. The values calculated from the formulas adopted in the experimental part are based on the formula for glycol lignin derived in an earlier paper (1).

Diazomethane-methylated glycol lignin was treated with phenol in a similar manner, and here also it was found that, with each lignin unit containing six methoxyl groups present in the diazomethane-methylated glycol lignin, three phenol molecules react to give a phenol condensation product containing three (new) phenolic hydroxyl groups, as shown by formation, on benzoylation, of a benzoylated phenol methyl glycol lignin containing seven benzoyl groups.

Finally it was of interest to ascertain whether the remaining three free hydroxyl groups in glycol lignin play any part in the condensation reaction with phenol. Fully methylated glycol lignin (OCH_3, 31.5%) was therefore condensed with phenol in the usual manner. In the first experiment the reaction product was not purified immediately, and it was found later, from the analytical data, that approximately two methoxyl groups had been split off, a fact confirmed by the subsequent methylation experiment with diazomethane in which the three new phenolic hydroxyl groups were methylated

(Formula V). On benzoylation of the latter product in pyridine solution with benzoyl chloride another methoxyl group was removed and substituted by a benzoyl group as shown by analysis. This was also confirmed by the strong smell of methyl benzoate in the precipitated product. For a compound containing eleven methoxyl and two benzoyl groups, the calculated methoxyl value is 22 9%; for one containing ten methoxyl and three benzoyl groups the calculated methoxyl value is 19.6%. The latter value agrees very well with that found. In a second experiment, in which the product was worked up immediately, a phenol glycol derivative was obtained which still contained all the original methoxyl groups.

In recent publications (3, p. 136; 5) the suggestion has been made that lignin contains oxygen rings of the catechin, pyrone or flavone types. It seemed of interest, therefore, to examine the behavior of quercetin towards phenol and anhydrous hydrogen chloride under the same conditions as those used in the preparation of phenol lignin. No condensation was found to occur, thus indicating that the reaction with phenol is due to the presence of groupings other than those of a flavone type.

Experimental

Action of Phenol on Glycol Lignin

Glycol lignin (2 gm.) was dissolved in phenol (25 gm.), the solution heated on the water bath to 80° C., and 5 cc. of an ether solution containing 5% anhydrous hydrogen chloride added. The reddish-brown solution immediately turned a violet-brown. This solution was heated for 10 min., and an additional 2 cc. of the ether-hydrogen chloride solution was added. Heating was then continued for 10 min., and the same amount of the ether-hydrogen chloride solution was again added. After heating for a further period of 10 min. the phenol was distilled off as much as possible under reduced pressure at a temperature not over 85° C. The residue was dissolved in methyl alcohol and the solution poured into distilled water, the powdery precipitate filtered, washed with water and dried in a desiccator over sodium hydroxide and sulphuric acid. Yield of crude phenol compound, 2.8 gm. It was dissolved in dioxane, the solution centrifuged and filtered, and the product precipitated by adding the solution dropwise to dry ether, and stirring vigorously. It separated out as a fine light-violet-brownish powder, which was washed twice with ether, then three times with petroleum ether, dried and analyzed. Found: OCH_3, 13.1%*. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OCH_2CH_2OH) . 3C_6H_5OH$, [1198.6] (Formula I): OCH_3, 13.0%.

Repeated phenolation brought about no change in composition. The phenol glycol lignin is soluble in dioxane, acetone, pyridine, dilute sodium hydroxide solution, insoluble in benzene, ether, petroleum ether and water.

In a second experiment 7 gm. of glycol lignin was phenolated in the same manner. Yield after two phenolations, 7.5 gm. Found, OCH_3, 13.5%.

*No correction has been applied for the slight increase in value due to the presence of the glycol radical, as this falls well outside the limit of experimental error for the products in question.

Methylation of Phenol Glycol Lignin with Diazomethane

Phenol glycol lignin (Formula I) (2 gm.; OCH_3, 13.5%) was twice methylated and was then found to be no longer acted upon by the methylating reagent. Found: OCH_3, 23.1%. Analysis after a third methylation:—Found: OCH_3, 23.2%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3OCH_2CH_2OH . 3C_6H_5OCH_3$, [1254.6] (Formula II): OCH_3, 22.3%.

Acetylation of Phenol Glycol Lignin Premethylated with Diazomethane

Diazomethane-methylated phenol glycol lignin (1.3 gm.) was dissolved in dry pyridine (15 cc.). Acetic anhydride (10 cc.) was added, and the mixture allowed to stand at room temperature for 40 hr. It was poured on to ice, the precipitated product filtered and purified by precipitating from dioxane solution into ether. Found: OCH_3, 21.2%.

Benzoylation of Phenol Glycol Lignin

Phenol glycol lignin (1 gm.) was benzoylated using 10 cc. of pyridine and 3 gm. of benzoyl chloride at room temperature. After 48 hr. the mixture was poured on to ice and the solution extracted with chloroform. The chloroform solution was washed successively with dilute sulphuric acid, water, potassium bicarbonate solution, and water, and was finally dried with magnesium sulphate. The product was precipitated by pouring the chloroform solution into dry ether, from which it separated out as a fine, dry, brown powder. Found: OCH_3, 7.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCOC_6H_5)_4 (OCH_2CH_2OCOC_6H_5) . 3C_6H_5OCOC_6H_5$, [2030 8]: OCH_3, 7.6%.

Phenol Compound of Glycol Lignin Premethylated with Diazomethane

Glycol lignin (2 gm.) was premethylated with diazomethane and then phenolated in the same manner as that used with glycol lignin and the crude product (2.5 gm.) purified, using dioxane and ether. The dioxane ether solution was completely colorless. Found: OCH_3, 16 1%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3OCH_2CH_2OH . 3C_6H_5OH$, [1212.6]: OCH_3, 15.4%. The product has the same solubility relations as the corresponding glycol lignin derivative.

Benzoylation of the Phenol Derivative of Glycol Lignin Premethylated with Diazomethane

The above-mentioned phenol derivative of the premethylated glycol lignin (1 gm.) was benzoylated and purified as described above for the benzoylated phenol glycol lignin. Yield, 1.1 gm. Found: OCH_3, 9.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OOCC_6H_5)_3(OCH_2CH_2OOCC_6H_5) . 3C_6H_5OOCC_6H_5$, [1940.9]: OCH_3, 9.6%. The product is a finely divided, light-brown powder, soluble in dioxane, acetone, pyridine, glacial acetic acid, and insoluble in ether, petroleum ether, water and dilute sodium hydroxide.

Phenol Derivative of Fully Methylated Glycol Lignin

Experiment I

Fully methylated glycol lignin (2.5 gm.) was dissolved in 25 gm. of phenol and the solution heated to 80° C., and 2 cc. dry ether containing 2.5% anhydrous hydrogen chloride added. After 10 min., 0.5 cc. of the ether-hydrogen chloride solution was added and the same amount again after a further 10 min. After heating for 30 min. in all, since the mixture could not be worked up the same day, it was allowed to stand overnight. The phenol was then distilled off, the residue dissolved in a mixture of methyl alcohol and acetone (1 : 1) and the product precipitated by pouring the solution into distilled water. The crude product (2.8 gm.) was purified from dioxane and ether. Found: OCH_3, 20.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OCH_2CH_2OCH_3) . 3C_6H_5OH$, [1268.6]: OCH_3, 24.45% Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OH)_2(OCH_2CH_2OCH_3) . 3C_6H_5OH$, [1240.6] (Formula IV): OCH_3, 20.1%. This value is in agreement with the assumption of a loss of two methoxyl groups during the phenolation.

The product was then methylated with diazomethane. The above-mentioned phenol compound of fully methylated glycol lignin (1.75 gm.) was methylated repeatedly in dioxane solution with diazomethane and the product purified, using dioxane and ether. Prior to analysis it was washed twice with ether, three times with petroleum ether and dried. Yield, 1.8 gm. Found: OCH_3, 26.7%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OH)_2 . OCH_2CH_2OCH_3 . 3C_6H_5OCH_3$, [1282.7] (Formula V): OCH_3, 26.6%.

A portion (0.7 gm.) of the diazomethane-methylated product was benzoylated by dissolving it in a mixture of 6 cc. pyridine and 3 cc. of benzoyl chloride. After it had stood for 48 hr. at room temperature, the product was poured on to cracked ice. A sticky mass separated out which smelled strongly of methyl benzoate and did not solidify even after washing with water. On mixing with ether the product solidified, and the powdery product was filtered, dried, and purified from dioxane and ether. Yield, 1 gm. Found: OCH_3, 19.6%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OOCC_6H_5)_2 . OCH_2CH_2OCH_3 . 3C_6H_5OCH_3$, [1490.6]: OCH_3, 22.9%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OOCC_6H_5)_3 . OCH_2CH_2OCH_3 . 3C_6H_5OCH_3$, [1580.7] (Formula VI): OCH_3, 19.6%. The methoxyl value found is seen to be in good agreement with the assumption of the removal of one methoxyl group and its replacement by a benzoyl group together with benzoylation of the two free hydroxyl groups.

Experiment II

Fully methylated glycol lignin (2.5 gm.), was dissolved in 20 gm. of phenol, the solution heated to 80° C. and 1 cc. of dry ether containing 2.5% of hydrochloric acid added. The mixture was treated in the same manner as in Experiment I. After the reaction was finished, the excess of phenol was distilled off *immediately*, the residue dissolved in acetone and the reaction product precipitated by adding the solution dropwise to distilled water. The yellowish-brown precipitate was filtered and dried (yield, 3 gm.). It was dissolved in 30 cc. of dioxane and precipitated in well stirred, dry ether. Found: OCH_3, 24.1%. The methoxyl value did not change on repeating the phenolation, as shown by the following figures:—Found: OCH_3, 24.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OCH_2CH_2OCH_3) . 3C_6H_5OH$, [1268.6] (Formula VII): OCH_3, 24.4%.

Methylation of Phenol Diazomethane-methylated Glycol Lignin (Formula III) with Dimethyl Sulphate and Sodium Hydroxide

The above-mentioned phenol diazomethane-methylated glycol lignin (3 gm.) was methylated further in acetone solution with dimethyl sulphate and sodium hydroxide (30%) at room temperature. After the first methylation the acetone solution was separated from the aqueous layer and the product remethylated in the same way. A sample was then isolated and purified. Found: OCH_3, 29.9%.

This value did not change after treatment of the product with acetic anhydride and pyridine, indicating the absence of free hydroxyl groups. Yield, 3 gm. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9OCH_2CH_2OCH_3 . 3C_6H_5OCH_3$, [1310.7] (Formula VIII): OCH_3, 30.7%.

Action of Phenol on Quercetin in Presence of Hydrochloric Acid

Quercetin (2 gm.) was suspended in 20 gm. of molten phenol, the mixture heated in a water bath to 85° C. and then 5 cc. of ether containing 0.03 gm. anhydrous hydrogen chloride added. The mixture was maintained for 10 min. at the same temperature and shaken frequently. A second 5 cc. of the ether–hydrogen chloride solution was then added, and the mixture heated for a further 10 min. This was followed by a third similar treatment, the total time of heating at 85° C. being 30 min. No such change in the color of the solution or of the quercetin took place as was observed in the case of the lignin derivatives. The phenol was distilled off under reduced pressure, the yellowish powdery residue washed with water and dried in a desiccator over sulphuric acid. Yield, 2 gm.; m.p., 310° C.; m.p. of quercetin, 312–313° C.; mixed m.p., 311° C. The quercetin was recovered unchanged.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XVI. PHENOL LIGNIN FROM SPRUCE WOOD, FROM FREUDENBERG SPRUCE LIGNIN AND WILLSTÄTTER SPRUCE LIGNIN[1]

BY IRENE KOERBER BUCKLAND[2], FRITZ BRAUNS[3] AND HAROLD HIBBERT[4]

Abstract

The condensation of lignin with phenol by treatment of spruce wood meal with this solvent, using hydrogen chloride as catalyst, yields *two* chemically different phenol lignins, namely, an ether-insoluble and an ether-dioxane–soluble phenol lignin, in a ratio of approximately 3 to 1. Duplicate preparations gave the same yields of these two fractions, analyses of which gave concordant results, indicating homogeneity and constancy of composition.

The analytical results of the ether-insoluble phenol lignin, and of its methylated and acetylated derivatives, can be interpreted on the basis of the Brauns–Hibbert formula for the "native" lignin unit. It is found, in this way, that the ether-insoluble phenol lignin contains *three* new free phenolic hydroxyl groups capable of methylation with diazomethane, while one phenol group has reacted with one hydroxyl group in the lignin unit with formation of a phenyl-oxygen ether linkage.

The analytical results of the ether-dioxane–soluble phenol lignin indicate that a much larger quantity of phenol has condensed with the "native" lignin building unit than in the case of the ether-insoluble fraction. The exact number of phenol molecules reacting to form this condensation product has not been determined experimentally although calculations based on analytical data point to a number as large as 15 or 21.

The phenol condensation products were obtained from Freudenberg and Willstätter lignins in nearly quantitative yield and found to differ from the directly extracted phenol lignin in that neither of them could be resolved into two fractions, thus indicating that some change had taken place in the native lignin during the isolation process. The Brauns-Hibbert formula can also be applied to interpret the experimental data in both cases. These lignins appear to contain the same fundamental building unit as the ether-insoluble phenol lignin fraction isolated directly from spruce wood, with the difference that the former probably have one additional hydroxyl group capable of acetylation and diazomethane-methylation.

The correlation found to exist in the present investigation between the phenol condensation products from native spruce lignin, isolated Freudenberg lignin and Willstätter lignin is regarded as providing definite experimental evidence indicating the presence of a chemical unit common to various lignins. The phenol condensation products, it is considered, may serve as valuable reference compounds for proving the identity of lignins obtained from different sources and by use of different chemical reagents.

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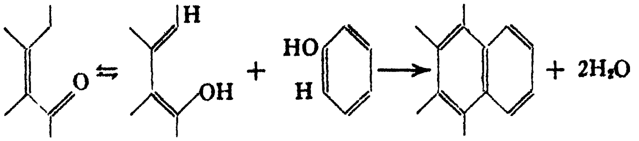
Introduction

This communication is the first of a series to be published on the chemistry of phenol derivatives of spruce lignin, and a brief historical survey on phenol lignin seems desirable.

The basis of all the work on the extraction of lignin from wood by means of phenols is to be found in Bühler's patent (5, 6) relating to the isolation of a pure cellulose from wood. Bühler found that phenols at a temperature greater than 150° C. dissolve the resins, lignified material and other so-called incrusting materials in wood, leaving the cellulose as an insoluble residue. Increased pressure and temperature promoted the solvent action (7). Renker (24, p. 81) found that *p*-cresol was a good solvent but not as efficient as phenol. Hartmuth (12) in 1919 discovered that small amounts of hydrochloric acid catalyzed the rate of extraction. Kalb and Schoeller (17, 18) in 1920 took out a patent for converting lignified vegetable tissues into soluble material by means of phenol in the presence of traces of mineral acids. They claimed that the catalyzing effect of the acid was due to the presence of hydrogen ions. Legeler (21) showed that 0.03% hydrogen chloride (calculated on the weight of phenol used) is sufficient to bring about a solution of the lignin in 15 min., while without the acid the lignin extraction occupied more than seven hours. The best results were obtained with anhydrous phenol. The first systematic study of phenol lignin was made by Hillmer (14). He determined the solubility of "native," unchanged lignin as present in wood, as well as that of an isolated lignin (Willstätter), in a comprehensive series of aromatic hydroxy derivatives, both in presence and absence of mineral acid. The effect of the substitution of groups in phenols on the solubility of lignin was also studied. In general, Hillmer's experiments show that the delignification of wood, or the solution of isolated lignin, is best effected by the use of (i) a phenol with two hydroxyl groups, (ii) a hydroxy benzoic acid, or (iii) a phenol containing a nitro, chlorine, bromine, or aldehyde group, meta or para to the hydroxyl.

The general method for the preparation of phenol derivatives of lignin consists in treating the dried wood meal, or isolated lignin, with 10 parts of molten anhydrous phenol in the presence of small amounts of catalyst. Legeler (21) used an ether solution containing 0.03% hydrogen chloride calculated on the weight of phenol, while Hillmer (14) used 1% of a mineral acid or 0.2% iodine as catalyst.

The mechanism of the reaction between phenol and lignin is far from settled. Hillmer (14) offered the following theory. When, for example, *p*-cresol, *o*-nitrophenol or *m*-hydroxy benzoic acid is used to dissolve the lignin, then, in the nitrophenol lignin, nitrogen can be detected; in the chlorphenol lignin, chlorine; and, in the *m*-hydroxy benzoic acid lignin, a carboxyl group. It was found that only those compounds containing a free phenolic hydroxyl group are capable of reacting in this way. Hillmer (14) suggested that there exists in the lignin complex a reactive oxygen atom in the form of a ketone, aldehyde or hydroxyl group. He assumes that there is a keto group present capable of existing in an enol form in order that the phenol molecule can condense with this by splitting out two molecules of water to form a new benzene nucleus.



In this case the number of free (OH) groups is the same before and after conversion of the lignin into the phenol derivative. But it has been shown definitely that there are new phenolic hydroxyl groups present in phenol lignin. The reaction must therefore be postulated in such a way that the phenolic hydroxyl remains unchanged. The assumption that there is a loose molecular combination between the phenol and the lignin is disproved by the fact that up to the present time it has been impossible to decompose the phenol lignin into the original compounds by solvents, or mild chemical processes. Wedekind and co-workers (29) suggested that the hydrogen atom para to the hydroxyl group in the phenol reacts with the lignin complex. This reaction can be postulated as taking place either by the saturation of a double bond in the lignin complex, the para hydrogen going to one carbon of the double bond and the phenol residue to the other, or by the condensation of the para hydrogen of the phenol with a hydroxyl group of the lignin molecule with the elimination of water. The first view is supported by the work of Schrauth and Quasebarth (26) on the condensation of phenols with cyclic hexenes. They found, by using the method of Königs (19, 20), that it was possible to condense cyclohexene with phenol to give a *p*-cyclohexene phenol. The more highly substituted cyclic hexenes and terpene derivatives gave increasing yields of alkali-soluble phenol condensates. Cross and Bevan (8), Jonas (15), and Schrauth (25, 26) have all presented formulas for lignin with such ring systems. On the other hand, Niederl and Smith (23, 28) have studied the addition of phenol to ethylenic linkages as found in unsaturated ketones, alcohols, ethers, esters, aldehydes, and hydrocarbons. In all cases a catalyst such as concentrated sulphuric acid is essential for the reaction. According to their experiments no hydrogenated ring system such as that assumed by Konigs and by Schrauth and Quasebarth is necessary to explain the addition of phenol to unsaturated compounds.

The mechanism of the reaction between phenol and lignin has not yet been definitely proved. However, there is no doubt that the phenol reacts with the lignin in such a way that new phenolic hydroxyl groups appear in the lignin derivative, as proved in the present paper.

Discussion

On extraction of spruce wood meal with phenol in presence of a trace of hydrochloric acid, the lignin is completely dissolved and a crude phenol lignin is obtained in a yield of over 140%. This crude lignin can be fractionated by the use of dioxane and ether into two fractions, an ether-insoluble fraction

(A) (75%) and an ether-soluble fraction (B) of about 25%. When toluene sulphonic acid is used as catalyst a higher yield of ether-insoluble phenol lignin with the same methoxyl content as for Phenol Lignin A is obtained, but the reaction takes place much more slowly. The high yield of phenol lignin shows that a large amount of phenol must have reacted with the lignin, and the question arises as to the number of phenol groups introduced, and as to the manner in which the phenol groups are combined with the lignin molecule. Since it is known that in the action of methyl alcohol (3), glycol (11), glycol monomethyl ether (11), and cyclohexanol (1), one molecule of these alcohols reacts with the lignin to form an ether, it seems probable that *one* molecule of the phenol also reacts in the same manner. The remaining phenol molecules reacting with the lignin apparently enter the lignin complex in such a way that the phenolic hydroxyl groups are left uncombined. The number of these groups entering the lignin molecule in nuclear condensation was determined by Brauns and Hibbert (4). They showed that glycol lignin methylated with diazomethane, as well as the fully methylated glycol lignin, gave with phenol, under the conditions used in the preparation of phenol lignin, phenol condensation derivatives in which three new phenolic hydroxyl groups have been introduced into the respective phenol lignin condensation products. The whole matter becomes clearer on applying the formula proposed by Brauns and Hibbert as a working hypothesis. These authors derived from their analytical results a building unit for native lignin of $C_{42}H_{32}O_6(OCH_3)_5(OH)_5$ with a molecular weight of 872 (2). For a phenol lignin with one phenol-ether linkage and three phenol groups present in nuclear condensation, the following formula may be postulated: $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OC_6H_5).3C_6H_5OH$.* The theoretical methoxyl content of such a phenol lignin unit is 12.6%, whereas that actually found for the ether-insoluble Phenol Lignin A is only 10.3%, and that for the ether-dioxane–soluble Phenol Lignin B is 5 3%. If it is assumed, however, that in the preparation of phenol lignin from spruce wood meal, one methoxyl group is split off, the theoretical methoxyl value of the product $C_{42}H_{32}O_6(OCH_3)_4(OH)_5(OC_6H_5)\ 3C_6H_5OH$ would be 10.2%. As a matter of fact, all the analytical values found for the various derivatives from the Phenol Lignin A are then found to be in agreement with the above formula. Phenol Lignin A can be readily acetylated with acetic anhydride and pyridine, resulting in a theoretical decrease in methoxyl content from 10 2 to 8.0% (found 7.9%) and an acetyl value of 22 2%; found, 23.1%. Methylation with diazomethane brings about an increase in methoxyl from 10.3 to 21.6%, a value which agrees with that calculated for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3OC_6H_5.\ 3C_6H_5OCH_3$ and corresponding to the entrance of five new methoxyl groups (21.7%). The diazomethane-methylated Phenol Lignin A still contains free hydroxyl groups capable of acetylation and methylation. The fully methylated compound was prepared in two ways, *(a)* by the simultaneous deacetylation and methylation of the diazomethane-methylated and acetylated Phenol Lignin A; and *(b)* by simultaneous deacetylation and methylation of the fully acetylated Phenol Lignin A. The average methoxyl content of both the products so obtained is 28.1%, while the value calculated on the basis of the proposed formula $C_{42}H_{32}O_6(OCH_3)_9(OC_6H_5).3(C_6H_5OCH_3)$ is 28.0%.

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* *Recent experiments also permit the possibility that the phenol, after splitting an oxygen ring, reacts with ether formation, forming a new phenolic hydroxyl group.*

The ether-soluble fraction, B, has a much lower methoxyl content (5.3%), and the assumption was first made (2) that in the case of Phenol Lignin B additional methoxyl groups have been removed. As a matter of fact if it is assumed that three instead of one are split off, (as in the case of Phenol Lignin A) the calculated value is 5.3%, the same as that found. This assumption, however, is disproved by the elementary analysis, as well as by the analyses of the derivatives. The high carbon content and the low methoxyl values show that considerably more phenol must have reacted with the lignin. The quantity of phenol that has reacted with one molecule of lignin can be calculated approximately from the analytical data. The probable assumption is that, as with Phenol Lignin A, one molecule of phenol reacts with the native lignin with formation of a phenol ether, one methoxyl group being split off in the process. Such an ether would have the following empirical formula: $C_{42}H_{32}O_6(OCH_3)_4(OH)_5(OC_6H_5)$, [934]. The carbon content of this hypothetical compound is 66.8%. The carbon content of phenol is 76.6% and that found for Phenol Lignin B is 72.8%. If x molecules of phenol (m. w. 94) react with one molecule of the hypothetical lignin phenol ether without loss of water to give Phenol Lignin B, the molecular weight of the latter will be $(94x + 934)$. Since the carbon contents of phenol, the hypothetical phenol lignin compound, and of Phenol Lignin B are known, namely 76.6%, 66.8% and 72.8%, respectively, the following equation can be postulated:

$$\left(94x \times \frac{76.6}{100}\right) + \left(934 \times \frac{66.8}{100}\right) = (94x + 934) \times \frac{72.8}{100}$$

from which $x = 15.6$ (based on four OCH_3 groups).

When the methoxyl content is used as the basis for calculation instead of the carbon content x would be 14.7 and 21 for four and five methoxyl groups respectively. For a phenol lignin with 15 molecules of phenol and 5 methoxyl groups, a methoxyl value of 6.6%, instead of the found value of 5.3%, is calculated. If, however, as in the case of Phenol Lignin A, one methoxyl group is split off during the phenolation, the calculated methoxyl value becomes 5.3%, and the calculated carbon content 72.7%, in agreement with the experimental values found. The exact number of phenol molecules in combination with the lignin cannot be determined on the basis of the experimental results at present available. Some of these, for example those relating to the diazomethane-methylated product, are in better agreement with the theory that Phenol Lignin B is composed of one molecule of lignin phenol ether and 15 molecules of phenol, while others, for example the acetylated derivative, agree closely with a Phenol Lignin B with 21 molecules of phenol. The fully methylated compound does not provide any clue to the structure since its methoxyl value is very close to that of methylated phenol.

It is apparent that no great value can be attached to these conclusions in view of the very high molecular weights of the products involved, with consequent inability to apply the analytical results for carbon, hydrogen and methoxyl values in a satisfactory manner.

Hillmer (14) and Hochfelder* mention the presence of a second phenol lignin but they did not isolate the pure product.

There is no doubt that Phenol Lignin B is related in some way to the original lignin. The phenol cannot be loosely bound or adsorbed on the lignin, or otherwise it would certainly be removed during the methylation with dimethyl sulphate and alkali. The experimental results obtained in the present series of methylation reactions permit, however, of no justifiable speculation concerning the mechanism of the condensation of the phenol with the lignin to form the Phenol Lignin B.

Phenol Derivatives of Isolated Lignins

Phenol derivatives of isolated lignins were first made by Hillmer (14), using Willstätter lignin and alkali lignin, while Wedekind (29) condensed alkali lignin (lignic acid) and metalignin (the product obtained by extraction of spruce wood with 5% sodium hydroxide in an autoclave at 170° C.), but neither investigated the phenol products obtained. Willstätter† as well as Freudenberg lignin (9, 10), when not dried previously, go readily into solution when heated with phenol. On treatment of the water-free suspension of the lignin in phenol with traces of hydrochloric acid at 80–90° C., the lignin swells and gelatinizes. After further heating, the product liquefies again and the lignin goes slowly and completely into solution. The isolated phenol lignin derivatives have the same properties as the Phenol Lignin A described above, but they differ from the latter in their higher methoxyl content, a difference which corresponds, on the basis of a molecular weight of about 1230, to one methoxyl group, thus indicating that in the case of the isolated lignins no methoxyl groups are split off. From these new phenol lignin derivatives, partially methylated, acetylated, and completely methylated derivatives were prepared. It is remarkable that the phenol derivatives of Freudenberg lignin have a slightly lower methoxyl content than those of the Willstätter lignin. This may be due to the fact that the former still contains the methylene oxide group—an observation which is confirmed in the following paper (Part XVII). It is of especial interest that on methylation of both phenol derivatives with diazomethane, products are obtained having a higher methoxyl content than the corresponding derivative of Phenol Lignin A.

This higher methoxyl value corresponds approximately with one methoxyl group, but no explanation can be given at the present time for the appearance of a new hydroxyl group capable of methylation with diazomethane. Also, the methoxyl content of the fully methylated phenol derivatives of Freudenberg and of Willstätter lignin is higher than that of Phenol Lignin A. Klason

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**Dissertation, Munich 1915. Reviewed by Melander (22).*
†See Reference (16).

lignin prepared according to the method of Hawley and Harris (13)* shows a behavior entirely different from that of Freudenberg and of Willstätter lignin. In spite of a higher concentration of the catalyst and the application of a higher temperature it does not go into solution with phenol. It was therefore not investigated further.

Experimental

General Procedure for the Purification of Phenol Lignin Derivatives

In order to avoid repetition, the general procedure for the precipitation and purification of the phenol lignin derivatives will be described in detail and then referred to as occasion arises. All the lignin derivatives synthesized were purified by successive precipitations until the methoxyl values of the product were found to be constant within the allowable experimental error (0.2%) for semi-micro Zeisel determinations on amorphous substances.

The crude, dry phenol lignin derivative is dissolved in about ten times its weight of pure dioxane, the lignin solution centrifuged, filtered through a white ribbon filter (Schleicher and Schüll) and then added drop by drop to the rapidly and constantly stirred precipitating medium. Vigorous and efficient agitation is necessary in order to obtain a finely divided light-colored product. In general, a 10% solution of the lignin derivative will be found to require at least 8 to 10 volumes of precipitant. The precipitate is separated by centrifuging and the supernatant liquid decanted from the loose cake. The lignin precipitate is now mixed with more of the fresh, dry precipitating liquid (in general 200 cc. to about 5 gm. lignin), and the mixture well stirred before the addition of more lignin solution. This procedure is repeated until all of the lignin has been precipitated; the product is then washed by agitation with at least two successive portions of the precipitating liquid (or until, after centrifuging, the supernatant liquid is colorless). The solid material is then stirred with several successive portions of low boiling petroleum ether (b.p. 30–50° C.), in order to remove the remaining traces of the precipitant occluded by the solid. When ether is used as a precipitant, great care must be taken to insure the removal of the last traces of it by stirring the solid products for at least half an hour with each fresh portion of the petroleum ether. It is usually convenient to allow the precipitate to stand overnight in fresh petroleum ether before the final centrifuging.

The washed products are centrifuged and dried, without transferring them from the centrifuge jar, in a vacuum desiccator (12–15 mm.) over concentrated sulphuric acid and potassium hydroxide sticks. Prior to analysis, they are subjected to a final, thorough drying in an Abderhalden apparatus in the presence of phosphorus pentoxide at approximately 2 mm., the temperature employed varying with the nature of the material in question.

Preparation of Phenol Lignin

The method used was a modification of that employed by Hillmer (14) and Wedekind (29).

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*See also Reference (27).

The wood meal used in this and similar experiments was spruce wood ground to 100 mesh and pre-extracted with an alcohol-benzene mixture (1 : 1) to remove fats and resins, followed by water to remove residual sugars. It was dried for several days at 60° C. in a vacuum oven at approximately 20 mm. pressure.

Pure anhydrous phenol (2000 gm.) was placed in a three-litre, three-necked flask equipped with a mechanical stirrer and a dropping funnel. The phenol was heated to 80° C., and 180 gm. woodmeal, which had been heated to the same temperature in a drying-oven for about 24 hr., was added.

An anhydrous ether solution (200 cc.) containing 12 gm. of hydrogen chloride was added slowly during a period of about 10 min. through the dropping funnel, the end of which was placed below the surface of the molten phenol. The mixture was stirred constantly and the temperature maintained between 80° and 90° C. The color of the mixture changed gradually from a light yellow to a brownish purple. At the end of half an hour, the phenol was distilled off under reduced pressure in an atmosphere of nitrogen, using an oil pump. The temperature of the water bath during the distillation was kept lower than 80° C. The residual product was a dark brown tarry solid. It was dissolved in 300 cc. of pure methyl alcohol at room temperature. The dark brown solution was centrifuged and the filtered lignin solution precipitated by adding the clear methyl alcohol solution dropwise to approximately four litres of distilled water, which was stirred vigorously. The light-brown solid that separated out was washed by decantation with water until the washings were clear, and then filtered on a Büchner funnel.

The residue left after the phenol treatment was extracted with methyl alcohol and centrifuged. This residue is the cellulose from the wood meal and, according to previous investigators, is almost pure. The alcoholic extract was concentrated under reduced pressure and the lignin precipitated as described above. The total yield of dry, crude phenol lignin was 121 gm. or 67% of the weight of the original wood meal taken. OCH_3, 6.4%.

Duplicate experiments gave approximately the same yield of crude phenol lignin with nearly the same methoxyl values (*i.e.*, 6.4, 7.0, 6.8% respectively in three different preparations).

Fractionation of Crude Phenol Lignin

The crude phenol lignin (OCH_3, 6.4%) was separated into (I) an ether-insoluble fraction (Phenol Lignin A) and (II) an ether-dioxane–soluble fraction (Phenol Lignin B) by the following procedure.

I. *Isolation of Ether-insoluble Phenol Lignin A*

Crude phenol lignin (30 gm.; OCH_3, 6.4%) was dissolved in 300 cc. of anhydrous, glycol-free, pure dioxane, giving a very dark reddish-brown solution. This was centrifuged to remove a small amount of insoluble material, filtered and precipitated by allowing the solution to drop into seven to eight times its volume of well stirred anhydrous ether. The lignin was precipitated as a fine light-brown product, while the supernatant ether solution was dark reddish-brown in color. It was then centrifuged, washed with three portions of dry ether, then with one portion of petroleum ether (b.p. 80–90° C.) and finally with two portions of low-boiling petroleum ether (b.p. 30–50° C.). The product was purified and dried as described under the general procedure for purification of lignin derivatives. The ether-insoluble Phenol Lignin A was obtained as a fine, very electrostatic, buff-colored powder; 17.5 gm. or 58% of the original crude phenol lignin was recovered as the ether-insoluble fraction. OCH_3, 8.9%.

Second purification. Phenol Lignin A (17.5 gm.) (product from the previous precipitation) was redissolved in 125 cc. of dioxane; the solution was centrifuged and the clear liquid added dropwise to 1500 cc. of dry ether. The precipitate was washed with ether, and then with high- and low-boiling petroleum ether (b.p. 80–90° C. and 30–50° C.). Yield, 16 gm. OCH_3, 9.5, 9.2%.

The third, fourth, and fifth purifications were carried out in the same manner as the second.

Fourth purification. Yield, 11.5 gm. OCH_3, 10.4, 10.4%.

Fifth purification. Yield, 10.5 gm. Found (ash-free basis): C, 68.99, 69.49, 68.76; H, 5.90, 6.03, 5.68; OCH_3, 10.4, 10.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_4(OH)_5(OC_6H_5).3C_6H_5OH$, [1216.5]: C, 69.00; H, 5.96; OCH_3, 10.2%.

The products from three preparations of phenol lignin from wood meal were purified separately and, in each case, gave ether-insoluble phenol lignin fractions having identical analytical values.

The ether-insoluble Phenol Lignin A is very soluble in dioxane, methyl and ethyl alcohols, acetone, pyridine, aqueous sodium hydroxide; soluble in warm amyl alcohol, methyl and ethyl acetates, glacial acetic acid; insoluble in water, chloroform, carbon tetrachloride, ammonium hydroxide, petroleum ethers, benzene, toluene, sodium bicarbonate and aqueous mineral acids.

II. *Isolation of Ether-Dioxane–soluble Phenol Lignin B*

The dark reddish-brown ether solutions remaining after the removal of the ether-insoluble Phenol Lignin A, together with the first two ether washings, were filtered and evaporated in a weighed flask under reduced pressure at 30° C. to remove excess dioxane. The dark brown tarry residue was dissolved in dioxane to give an approximately 10% solution, centrifuged to remove a small amount of insoluble material, filtered and precipitated by adding it dropwise to ether. The small flocculent precipitate of ether-insoluble material was isolated, purified and dried as described previously. The methoxyl value of the washed and dried product was 9.4%, showing that the material was impure Phenol Lignin A. The ether filtrate from this precipitation was again evaporated, dissolved in approximately the same amount of dioxane and filtered.

The ether-dioxane–soluble Phenol Lignin B was very difficult to obtain in solid form.

When the dioxane solution of the residue, which remained after evaporation of the ether, was precipitated in dry benzene, a somewhat flocculent, fine, light-brown product was obtained and the benzene acquired a yellowish-brown color. The insoluble material was stirred with several portions of benzene until the latter was no longer colored. The product was allowed to stand in petroleum ether (b.p. 30° to 50° C.) for about an hour with occasional stirring. The liquid was centrifuged from the solid product and the latter stirred with three more portions of petroleum ether. The final product, dried in the usual manner, was a fine light-brown powder.

The small amount of lignin left in the benzene-dioxane mixture resulting from the first precipitation of the Phenol Lignin B was recovered by evaporating off the bulk of the solvents under reduced pressure, filtering and adding the filtered solution dropwise to a large quantity of pure dry benzene. About one gram of material was thus isolated and added to the main product for further purification. Total yield—15 gm., or 50% of the crude phenol lignin.

The Phenol Lignin B was dried over phosphorus pentoxide at a temperature of 56° C. at 10–12 mm. for 36 hr. OCH_3, 4.9%.

This product was subjected to four consecutive reprecipitations, as described above, before the methoxyl value became constant.

Fourth purification. Found: C, 72 74, 72 87; H, 5.92, 6.0; OCH_3, 5.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OC_6H_5)\cdot 15C_6H_5OH$, [2358.4]: C, 72.8; H, 6.2; OCH_3, 5.4%.

Three preparations of crude phenol lignin were purified separately and in each case an ether-dioxane–soluble fraction was obtained having the same final methoxyl value.

Pure Phenol Lignin B is very soluble in dioxane, methyl, ethyl and amyl alcohols, methyl and ethyl acetates, acetone, pyridine, aqueous sodium hydroxide and glacial acetic acid. It is only *very slightly* soluble in pure ether, but is readily soluble when a small trace of dioxane is added. It is insoluble in water, chloroform, carbon tetrachloride, pure benzene, toluene, aqueous mineral acids and cold ammonium hydroxide.

Acetylation of Ether-insoluble Phenol Lignin A

Phenol Lignin A (8 gm.; OCH_3, 10 3%) was dissolved in 40 cc. of dry pyridine and 25 cc. of acetic anhydride added. The dark reddish-brown solution was allowed to stand for 36 hr. at room temperature. The solution was poured in a thin stream on to finely cracked ice. After the ice had melted, the light-brown precipitate was filtered off, washed with ice-cold water until free from pyridine and acetic acid, and dried. Yield, 10 gm.

Purification

The product was dissolved in 100 cc. of dry dioxane, centrifuged to remove a small amount of insoluble material, filtered and added dropwise to 1200 cc. of anhydrous ether. The light buff-colored precipitate was washed with four portions of anhydrous ether, followed by three of low-boiling petroleum ether.

The product was a very light buff-colored powder. Yield, 8 gm. OCH_3, 7.8%. It was then submitted to a second similar treatment and the resulting product analyzed.

Found: C, 66.8, 66.54; H, 5.44, 5.35; OCH_3, 7.9, 7.9; $COCH_3$, 23.0, 23.2%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_4(OCOCH_3)_5OC_6H_5.3C_6H_5OCOCH_3$,[1552.7]: C, 66.46; H, 5.66; OCH_3, 8.0; $COCH_3$, 22.2%.

Methylation of Ether-insoluble Phenol Lignin A with Diazomethane

Phenol Lignin A (10 gm.; OCH_3, 10.3%) was dissolved in 60 cc. of dioxane, and diazomethane (prepared by slowly dropping 30 cc. of a sodium glycolate solution, containing 6% sodium, into 15 cc. of nitroso-methyl urethane) was led into the solution. After about an hour, there was a vigorous evolution of nitrogen and the solution became noticeably lighter in color. The reaction mixture was allowed to stand for three hours, and was then treated with the same amount of diazomethane. Upon standing overnight, a gelatinous precipitate, presumably a polymer of diazomethane, had formed in the solution, which was then heated at 50° C. for half an hour and filtered. A sample was precipitated by adding the solution to ether. The light-colored precipitate was stirred with three consecutive portions of ether followed by two of petroleum ether (b.p. 30–50° C.) OCH_3, 19.9%.

The remainder was dissolved in dioxane and the combined solutions were remethylated with diazomethane. The solution was allowed to stand overnight at room temperature and then heated at 50° C. for half an hour. The gelatinous precipitate was centrifuged off and washed with two successive portions of dioxane. The product was isolated and purified as described in the general procedure above. Yield, 8 gm. OCH_3, 21.5%.

The product was redissolved and again treated with diazomethane, exactly as described above. The reaction product was isolated as above and yielded a very light buff-colored product. Since further treatment with diazomethane did not increase the methoxyl content, the product was considered completely methylated with respect to diazomethane. Yield, 7.8 gm. Ash, 0.38%. Found (ash-free basis): C, 70.56, 69.86, 71.05; H, 6.44, 6.35, 6.33; OCH_3, 21.6%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3(OC_6H_5).3C_6H_5OCH_3$, [1286.6]: C, 70.0; H, 6.42; OCH_3, 21.7%.

Acetylation of Phenol Lignin A, Premethylated with Diazomethane

The premethylated Phenol Lignin A mentioned above (5.5 gm.; OCH_3, 21.5%) was dissolved in 30 cc. of dry pyridine, 18 cc. of acetic anhydride added and the solution allowed to stand for 30 hr. at room temperature. It was poured in a thin stream on to a mixture of cracked ice and water with stirring. After standing for several hours, a fine light-brown precipitate settled out. This was filtered off and washed with ice water until free from pyridine and acetic acid. Yield, 4.5 gm.

The product was dissolved in dioxane, filtered and precipitated by adding the solution dropwise to dry ether. The fine buff-colored product was centrifuged off and washed with three portions of dry ether and two of petroleum ether (b.p. 30–50° C.). Yield, 4 gm. OCH_3, 18.9%.

The product was purified by three further similar precipitations. There was no change in methoxyl value found in the product from the last two precipitations. Found: C, 69.12, 69.37; H, 6 06, 5.95; OCH_3, 19.1, 19.1; $COCH_3$, 11 5, 11 1%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCOCH_3)_3(OC_6H_5).3C_6H_5OCH_3$,[1412 7]: C, 68 8; H, 6 2; OCH_3, 19.7; $COCH_3$, 9.1%.

Deacetylation and Methylation of Phenol Lignin A Premethylated with Diazomethane and Acetylated

The acetylated Phenol Lignin A (1 5 gm.), previously methylated with diazomethane, was dissolved in 20 cc. of acetone. Sodium hydroxide (40 cc.; 30%) and 15 cc. dimethyl sulphate were added dropwise during a period of one hour at 40–42° C. with constant stirring, keeping the solution slightly alkaline throughout. The mixture was stirred at 40° C. for another hour.

The acetone was then distilled off under reduced pressure, a brown solid separating out. It was ground up with water in a mortar, separated by filtration, and washed free from inorganic salts. A small sample of the dried solid was purified by solution in dioxane and precipitation with ether, and analyzed for OCH_3. Found: OCH_3, 24 3%. After three additional methylations the methoxyl content was found to be constant. Found: OCH_3, 27 3, 27.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OC_6H_5).3C_6H_5OCH_3$,[1328.7]: OCH_3, 28.0%.

Deacetylation and Methylation of Completely Acetylated Phenol Lignin A

Approximately 5 gm. of Phenol Lignin A, which had been completely acetylated using pyridine and acetic anhydride, was dissolved in 80 cc. of acetone and methylated as described in the previous experiment by use of 180 cc. of 30% sodium hydroxide and 80 cc. of dimethyl sulphate. The reagents were added in five equal portions at half-hour intervals, care being taken to keep the reaction mixture slightly alkaline throughout the reaction.

The acetone was then removed under reduced pressure, and the dark reddish-brown precipitate separating out was filtered off, ground to a fine powder, and washed free from inorganic salts. Found: OCH_3, 27.3%.

After a second and third methylation under the same conditions the methoxyl content was found to be constant. The resulting material was purified by solution in dioxane and precipitation with ether. Found: C, 71.40, 71.23; H, 6.50, 6 47; OCH_3, 28 2, 28 3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OC_6H_5).3C_6H_5OCH_3$,[1328.7]: C, 70.45; H, 6 68; OCH_3, 28 0%.

PREPARATION OF DERIVATIVES OF PHENOL LIGNIN B

Acetylation of Ether-Dioxane–soluble Phenol Lignin B

Ether-dioxane–soluble Phenol Lignin B (6 gm.; OCH_3, 5.3%) was dissolved in 40 cc. of dry pyridine and 25 cc. of acetic anhydride added. The solution was allowed to stand for 48 hr. at room temperature, and the reaction product isolated in the usual manner. It was purified from dioxane–petroleum-ether (b.p. 30–50° C.), from which it separated as a very light brown powder.

The product was purified twice from dioxane and petroleum ether. Yield, 5.4 gm. Found: C, 68.42, 68.14; H, 5.75, 5.77; OCH_3, 4.4, 4.4; $COCH_3$, 24.0, 24.6%.

Diazomethane Methylation of Ether-Dioxane-soluble Phenol Lignin B

Ether-dioxane–soluble Phenol Lignin B (8 gm.) was dissolved in 50 cc. of dioxane, and the solution treated with diazomethane, prepared from 15 cc. of nitroso-methyl urethane. A vigorous evolution of nitrogen took place and the solution became noticeably lighter in color. The next day it was subjected to a similar treatment. The reaction mixture was heated at 50° C. for 15 min., centrifuged and a small sample purified. OCH_3, 22.3%. Since the methoxyl values after the third and fourth methylations did not increase further, the product was precipitated twice by adding the dioxane solution dropwise to petroleum ether (b.p. 30–50° C.). Yield, 7.5 gm. Found: C, 72.97, 72.77; H, 6.79, 6.70; OCH_3, 22.9, 22.8%.

Acetylation of the Diazomethane-methylated Product

Approximately 6.5 gm. of methylated Phenol Lignin B was dissolved in 30 cc. of pyridine, and 18 cc. of acetic anhydride added. The solution was allowed to stand for 48 hr. at room temperature.

The product was isolated and purified as described for the acetylated Phenol Lignin B. Yield, 5 gm. Found: C, 70.58, 71.08; H, 6.30, 6.33; OCH_3, 21.5, 21.6; $COCH_3$, 2.4, 2 7%.

Deacetylation and Methylation of Ether-Dioxane–soluble Phenol Lignin B Premethylated with Diazomethane and Acetylated

Approximately 2 gm. of ether-dioxane–soluble premethylated and acetylated Phenol Lignin B was dissolved in acetone and treated with 26 cc. of dimethyl sulphate and 36 cc. of 30% sodium hydroxide as described for Phenol Lignin A. After five methylations the methoxyl content was constant.

The product was purified by adding the benzene solution dropwise to petroleum ether (b.p. 30–50° C.). The precipitated product was of a very light buff color. Yield, 1.4 gm. Found: C, 72.43, 72.17; H, 6.48, 6.58; OCH_3, 27.4, 27.3%.

In order to ascertain whether the substance was fully methylated it was treated with acetic anhydride and pyridine. No change in the methoxyl value occurred. The product therefore contained no free hydroxyl groups.

Preparation of Phenol Derivative of Freudenberg Lignin

Moist Freudenberg lignin (125 cc.) (10) was freed from water as far as possible by careful filtration, and the material mixed with 120 gm. of phenol. A portion of the phenol was distilled off under reduced pressure to remove the water present in the lignin. The mixture was then heated to 80° C., and 5 cc. of anhydrous ether containing 8% gaseous hydrogen chloride added. The product immediately became darker in color and the gelatinous mixture began to liquefy. At 10 min. intervals, two additional portions of 2.5 cc. of ether–hydrogen-chloride solution were added. The reaction mixture was heated for a total period of 30 min. and at the end of this time had formed a clear, dark reddish-brown solution. The excess phenol was distilled off completely under reduced pressure, using an oil vacuum pump, and the dark-brown residue dissolved in 75 cc. of methyl alcohol. The solution was centrifuged and the small residue washed with methyl alcohol. The weight of this dried methoxyl-free residue was 0.9 gm.

The combined methyl alcohol solutions were filtered and the phenol lignin compound precipitated by adding the methyl alcohol solution dropwise to distilled water with constant stirring at room temperature. The phenol Freudenberg lignin separated out as a fine light-brown powder. The crude product was filtered-off and dried. Yield, 13 gm. OCH_3, 11.4%.

This product was purified by several precipitations from dioxane and dry ether. The light-brown precipitate finally obtained was centrifuged off, washed by stirring with three successive portions of ether and finally with two portions of petroleum ether (b.p. 30–50° C.). Yield, 12.5 gm. Found: C, 68.39, 68.57; H, 5.88, 5.94; OCH_3, 11.7, 11.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OC_6H_5).\ 3C_6H_5OH$,[1230.6]: C, 69.2; H, 6.0; OCH_3, 12.6%.

Phenol Freudenberg lignin is very soluble in dioxane, methyl and ethyl alcohols, acetone, pyridine and aqueous sodium hydroxide. It is soluble in warm glacial acetic acid, amyl alcohol, but insoluble in ether, water, chloroform, carbon tetrachloride, and sodium carbonate.

Acetylation of Phenol Freudenberg Lignin

Two grams of phenol Freudenberg lignin was acetylated with 16 cc. of dry pyridine and 10 cc. of acetic anhydride and allowed to stand for 48 hr. at room temperature. The light-brown solid isolated by the usual procedure was dried and purified twice by solution in dioxane and precipitation with ether. It was washed finally with two successive portions of ether, followed by two successive portions of petroleum ether. Yield, 2 gm. Found: C, 66.83, 66.56; H, 5.53, 5.47; OCH_3, 9.2, 9.4; $COCH_3$, 21.6, 21.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OCOCH_3)_4(OC_6H_5).3C_6H_5OCOCH_3$, [1524.7]: C, 66.9; H, 5.8; OCH_3, 10.2; $COCH_3$, 19.7%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_5$-$(OCOCH_3)_5(OC_6H_5).3C_6H_5OCOCH_3$,[1566.7]: C, 66.6; H, 5.8; OCH_3, 9.9; $COCH_3$, 22.0%.

Methylation of Phenol Freudenberg Lignin with Diazomethane

Phenol Freudenberg lignin (8 gm.) was dissolved in 50 cc. of dioxane and diazomethane from 15 cc. of nitroso-methyl urethane introduced into the solution. A vigorous evolution of nitrogen took place and the solution became lighter in color. After three hours it was given a second similar treatment with diazomethane. After a third methylation the methoxyl content was constant. OCH_3, 23.6%.

The light buff-colored product was washed with three successive portions of petroleum ether (b.p. 30–50° C.). Yield of dried product, 6 gm. Found:

C, 70.64, 70.76; H, 6.31, 6.27; OCH_3, 23.5, 23.6%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3(OC_6H_5).3C_6H_5OCH_3$,[1286.5]: C, 69.9; H, 6.4; OCH_3, 21.7%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OH)_3(OC_6H_5).3C_6H_5OCH_3$,[1300.6]: C, 70.1; H, 6.5; OCH_3, 23.8%.

Acetylation of Phenol Freudenberg Lignin Premethylated with Diazomethane

Phenol Freudenberg lignin (5 gm.), premethylated with diazomethane, was dissolved in 30 cc. of pyridine and 18 cc. of acetic anhydride. The product, isolated in the usual manner, was purified by four precipitations from dioxane into ether. Yield, 4 gm. Found: C, 68.90, 68.90; H, 6.17, 6.15; OCH_3, 21.6, 21.7; $COCH_3$, 8.4, 8.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCOCH_3)_3(OC_6H_5).3C_6H_5OCH_3$,[1412.7]: C, 68.8; H, 6.2; OCH_3, 19.7; $COCH_3$, 9.1%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OCOCH_3)_3(OC_6H_5).3C_6H_5OCH_3$,[1426.7]: C, 68.9; H, 6.3; OCH_3, 21.7; $COCH_3$, 9.0%.

Deacetylation and Methylation of Phenol Freudenberg Lignin Premethylated with Diazomethane and Acetylated

Premethylated and acetylated phenol Freudenberg lignin (2 gm.) was dissolved in acetone and treated with 27 cc. of dimethyl sulphate and 36.5 cc. of 30% sodium hydroxide in the manner described for the fully methylated Phenol Lignin A. After the fifth methylation the methoxyl content was constant. The product was purified by two precipitations from dioxane and ether. Found: C, 70.1, 70.6; H, 6.5, 6.5; OCH_3, 29.1, 29.1%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OC_6H_5).3C_6H_5OCH_3$,[1328.7]: C, 70.4; H, 6.6; OCH_3, 28.0%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_{10}(OC_6H_5).3C_6H_5OCH_3$,[1342.7]: C, 70.5; H, 6.7; OCH_3, 30.0%.

Phenol Lignin from Willstätter Lignin

Lignin (21 gm.; OCH_3, 15.2%), dried in a vacuum desiccator and prepared according to Willstätter's method (16), was mixed with 130 gm. phenol, and the mixture heated with stirring to 80–85° C. A thick mass was formed which was very difficult to stir and to this 10 cc. of ether containing 2.5% gaseous hydrogen chloride was added. After 10 min. an additional 5 cc. of the ether-hydrogen chloride solution was added and the pasty product then began to liquefy. After a further ten minutes a third portion of 5 cc. of the ether-hydrogen chloride solution was added and the mixture heated another 10 min. The total volume of ether solution added was 20 cc., and time of heating, 30 min. at 80–85° C. All the lignin passed into solution and the excess phenol was then removed by distillation under reduced pressure. The residual, dark brown, tarry mass was dissolved in methyl alcohol and centrifuged, leaving 0.9 gm. of residue. The solution, about 100 cc., was filtered and the phenol lignin precipitated by adding the methyl alcohol solution dropwise to 2.5 of litres of distilled water. A light-brownish solid separated. The filtration of the cocoa-colored product took three to four days, and it proved impracticable to centrifuge the solution. This product was purified in a manner similar to that used for Phenol Lignin A. Yield of crude phenol lignin, 15 gm. OCH_3, 11.7%.

Purification

The crude phenol Willstätter lignin was dissolved in 200 cc. of dioxane, the solution centrifuged, filtered and the product precipitated by adding this solution dropwise to dry ether. The precipitate was allowed to settle, and the almost colorless supernatant solution decanted. The residual lignin was washed twice with dry ether, three times with petroleum ether, and finally dried. OCH_3, 12.3%.

It was further purified by a second similar treatment. Found: OCH_3, 12.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_5(OH)_4(OC_6H_5).3C_6H_5OH$,[1230.5]: OCH_3, 12.6%.

Acetylation of Phenol Willstätter Lignin

Purified phenol Willstätter lignin (2 gm.) was acetylated with acetic anhydride and pyridine in the customary manner and the crude product twice precipitated by pouring the dioxane solution into ether. Yield, 2.4 gm. OCH_3, 9.6%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_5(OCOCH_3)_5(OC_6H_5).3C_6H_5\text{-}OCOCH_3$,[1566.7]: OCH_3, 9.9%.

Methylation of Phenol Willstätter Lignin with Diazomethane

Phenol Willstätter lignin (6 gm.) was dissolved in 16 cc. of dioxane and diazomethane, prepared from 15 cc. nitroso-methyl urethane, introduced. After two such methylations a sample was isolated and purified, after drying in an Abderhalden at 110° C. (2 mm.). OCH_3, 23.6%. It was again remethylated. OCH_3, 23.9%.

This value did not increase after another methylation. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OH)_3(OC_6H_5).3C_6H_5OCH_3$,[1300.6]: OCH_3, 23.8%.

Acetylation of Phenol Willstätter Lignin Premethylated with Diazomethane

Premethylated phenol Willstätter lignin (4.5 gm.) was acetylated with 25 cc. of dry pyridine and 15 cc. of acetic anhydride. The crude acetylated product (4.8 gm.) was isolated and purified in the usual manner. The cream-colored, fine powder was dried in a vacuum desiccator over sulphuric acid and the sample for analysis further dried in the Abderhalden at 78° C. (2 mm.) OCH_3, 21.6%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OCOCH_3)_3(OC_6H_5).\ 3C_6H_5\text{-}OCH_3$,[1426.7]: OCH_3, 21.7%.

Deacetylation and Complete Methylation of Phenol Willstätter Lignin Premethylated with Diazomethane and then Acetylated

Phenol Willstätter lignin (2.5 gm.), premethylated with diazomethane and then acetylated, was dissolved in 25 cc. of acetone, and methylated with 25 cc. of dimethyl sulphate and 55 cc. of hydroxide (35%) at room temperature. After two such methylations a sample was isolated and purified. OCH_3, 29.8%.

After a third methylation the methoxyl content was 30.0% Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OC_6H_5).3C_6H_5OCH_3$,[1328.6]: OCH_3, 28.0%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_{10}(OC_6H_5).3C_6H_5OCH_3$,[1342.7]: OCH_3, 30.0%.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XVII. METHYLATION OF WILLSTÄTTER AND FREUDENBERG LIGNINS[1]

By Fritz Brauns[2] and Harold Hibbert[3]

Abstract

Both Willstätter and Freudenberg lignins when treated with diazomethane give methylated products containing one additional methoxyl group, calculated on the basis of a molecular weight of about 850 for native lignin. When heated with phenol in the presence of a small amount of hydrogen chloride, *both* diazomethane-methylated lignin derivatives are converted into soluble phenol lignin derivatives containing one more methoxyl group than the corresponding phenol derivatives prepared from original, untreated Willstätter and Freudenberg lignins. This higher methoxyl value is also shown by the former phenol lignins on acetylation. The diazomethane-methylated phenol lignin derivatives *prepared from diazomethane-methylated Willstatter and Freudenberg lignins* correspond with the diazomethane-methylated phenol lignin derivatives prepared from *original Willstätter and Freudenberg lignins.* Also the fully methylated derivatives prepared from the phenol diazomethane-methylated Willstätter and Freudenberg lignins correspond with those described previously (2). The difference in methoxyl value between the phenol derivatives obtained from Willstätter lignin and the corresponding derivatives from Freudenberg lignin of 0.8–2.1% may be due possibly to the presence in the Freudenberg lignin of a methylene oxide ring which is removed in the isolation of Willstätter lignin, thus giving rise to the higher methoxyl content in the methylated derivatives of the latter. The action of methyl alcohol on original, on diazomethane-premethylated, and on fully methylated Willstätter and Freudenberg lignins was also investigated.

Introduction

The nature of the changes taking place during the methylation of lignin is still an unsolved problem. It is well known that lignin can be readily methylated by the usual methylation reagents. For instance, Heuser and co-workers (12) were able to methylate spruce lignin, isolated according to the method of Willstätter, by suspending the product in 10% sodium hydroxide solution and adding dimethyl sulphate gradually at a temperature of 60° C. In this manner the methoxyl content was increased from 14.6 to 20.7%, and, by repeating the process, a product was finally obtained with a methoxyl content of 26.3%.

Urban (14) methylated a spruce lignin (isolated by means of hydrochloric acid and phosphoric acid) by use of 45% sodium hydroxide solution and dimethyl sulphate at 80–100° C. After 15 successive methylations the product had a methoxyl value of 28.2%. He found, however, that if the temperature during methylation did not exceed 25° C., after two methylations a product is obtained with 32.4% OCH_3. Freudenberg (6) showed that on treatment of a similar lignin preparation with an ether solution of diazomethane, the methoxyl content could be increased from 15.5 to 19.8%. Later (7) he corrected this value by reporting that the methoxyl increase amounted only to 2%. A similar result was obtained by Fuchs and Horn (10) who treated spruce wood meal with diazomethane and then isolated the methylated lignin with concentrated hydrochloric acid. This methylated lignin had a methoxyl content of 19.7%, while that of the lignin isolated by the use of concentrated hydrochloric acid and phosphoric acid from the original wood was 15.4%. They calculated from these results that on the basis of a molecular weight for lignin of about 800, it contains one hydroxyl group capable of methylation with diazomethane. It has been shown repeatedly that when lignin is extracted from spruce wood meal by means of alcohols in presence of hydrogen chloride as a catalyst, a lignin derivative is obtained which is soluble in dilute sodium hydroxide and which can be reprecipitated from such solution with acids. After treatment of methanol lignin with diazomethane, the methoxyl content increases from 21.6 to 24.8% (1). This methylated product is insoluble in sodium hydroxide and is stable towards warm sodium alcoholate, indicating absence of ester methoxyl groups capable of saponification. This indicates that there is present an acidic hydroxyl group capable of methylation with diazomethane. Since, on the one hand, Freudenberg (3, p. 122) contends that lignin prepared according to his method, by extraction of wood meal with cuprammonium hydroxide, contains no free phenolic hydroxyl group, while Fuchs (11), on the other hand, claims that in the preparation of lignin by alcoholysis, using methanol, ethanol, glycol, or glycol monoethers, a *new* phenolic hydroxyl group is formed by opening of an oxygen ring during the extraction process, it seemed advisable to re-investigate this matter.

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Spruce lignin was prepared according to the Willstätter (13) and Freudenberg (9) procedures and kept under water, since, if allowed to dry, the surface of the lignin particles becomes horny. Prior to use, the material was filtered by suction, the moist lignin mixed with cyclohexanol, the water removed by distillation under reduced pressure, and the last-mentioned process continued until pure cyclohexanol passed over. The swollen lignin thus obtained was finely ground by shaking the mixture with glass beads for several days. Such a suspension of finely divided lignin permits a thorough methylation with diazomethane. After six consecutive methylations, the cyclohexanol being replaced by acetone after the third methylation, a final methoxyl content of 21.3% for the Willstätter lignin and of 20.4% for the Freudenberg lignin was obtained. That methylation had occurred was indicated by the change in external appearance of both lignins from a brown to a light cream color. On treatment with phenol and hydrochloric acid each of the diazomethane-methylated products was converted into a soluble phenol lignin derivative containing, on the basis of a molecular weight for phenol lignin of 1230 (2), one additional methoxyl group as compared with the phenol derivatives of the original lignins (2). On methylation of these phenolated products with diazomethane, derivatives were obtained having the same methoxyl content as the diazomethane-methylated phenol lignin prepared from the original lignins (2). Also the acetylated and completely methylated derivatives show the same agreement with the corresponding derivatives described by Buckland, Brauns and Hibbert (2). It must, however, be noted that the methoxyl values of the Freudenberg lignin derivatives are somewhat lower than those of the Willstätter lignin. This may be due to the fact that possibly the Freudenberg derivatives still contain the methylene oxide ring (4, 5, 8), while it has probably been removed in the isolation of the Willstätter lignin, thus permitting an increased methylation with diazomethane.

When Willstätter and Freudenberg lignins, premethylated with diazomethane, are treated with methyl alcohol and hydrochloric acid, almost complete solution is obtained. The methanol lignin derivatives thus formed are found to differ from the methanol lignin prepared either by extraction of wood meal with methyl alcohol, or by the action of methyl alcohol on the original Willstätter or Freudenberg lignin, in having a higher methoxyl content. The actual value found is in agreement with that of the diazomethane-methylated methanol lignin which likewise is insoluble in sodium hydroxide, thus indicating absence of a free acidic hydroxyl group of a phenol type in the diazomethane-methylated Willstätter and Freudenberg lignins.

On methylation of diazomethane-premethylated Willstätter and Freudenberg lignins with dimethyl sulphate and sodium hydroxide at room temperature, fully methylated lignin derivatives are obtained.

Experimental

Methylation of Willstätter Lignin with Diazomethane

Willstätter lignin (OCH_3, 15.5%) which, after its preparation, had been kept under water, was filtered and the moist product transferred to a glass distilling flask, mixed with cyclohexanol, and the remaining water removed by distilling under reduced pressure. It is always necessary to add some fresh cyclohexanol during the distillation. When the cyclohexanol distils over free from water, the lignin is left as a very fine suspension in the solvent and is ready for methylation with diazomethane in the usual manner. Vigorous nitrogen evolution took place and after four methylations a sample was removed, filtered, washed with methyl alcohol, acetone, ether, benzene, dioxane, and petroleum ether. The product was then suspended in water, boiled for 15 min. and dried in an Abderhalden at 100° C./2 mm. The main portion was remethylated in the same way and another sample was purified and analyzed. OCH_3, 20.8%. The total product was then centrifuged, the cyclohexanol removed by washing with benzene, and the methylation repeated in benzene suspension. The benzene solution was still yellowish after two days, and the excess of diazomethane was then destroyed by adding a few drops of glacial acetic acid. The methylated lignin was filtered and washed successively with acetone, dioxane, and ether, then boiled for 15 min. with water and dried. Found: OCH_3, 21.2, 21.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$ [886.4] : OCH_3, 21.0%.

Willstätter lignin, after methylation with diazomethane, has a canary yellow color, is free from nitrogen and is insoluble in all solvents.

Action of Phenol and Hydrochloric Acid on Willstätter Lignin Premethylated with Diazomethane

Three grams of Willstätter lignin, premethylated with diazomethane (OCH_3, 21.2%), was suspended in 50 gm. of liquid phenol heated to 80° C. and 2 cc. of ether containing 2.5% of hydrogen chloride introduced under the surface of the phenol solution. The light-yellow color of the mixture turned light reddish-brown, the lignin began to swell, the mixture became more and more viscous and the product was finally gelatinized. After 10 min. an additional 1 cc. of the ether–hydrogen-chloride solution was added and after heating for about 30 min. at 80° C. the mixture again began to liquefy. After one hour the lignin had almost completely dissolved with formation of a clear, dark reddish-brown solution. This was heated for another hour, the phenol distilled off under reduced pressure and the residual syrupy product dissolved in a mixture of 50 cc. of equal parts of methyl alcohol and acetone. The solution was centrifuged and poured into 600 cc. of distilled water, forming a colloidal solution. In order to coagulate the lignin, 1–2 cc. of a saturated sodium sulphate solution was added and the mixture stirred for 10 min. The lignin compound separated out as a light-brown, flocculent precipitate which was filtered off, washed with distilled water and dried. Yield, 3.25 gm. OCH_3, 15.3%.

In the second experiment, 3.5 gm. of Willstätter lignin gave 4.5 gm. of the phenol compound (OCH_3, 15.8%).

The insoluble residues from both experiments were washed with a mixture of methyl alcohol and acetone, then with ether, and dried. Yield, 0.31 gm. or 4.8% of the total lignin used.

The combined phenolated lignins (7.3 gm.) were dissolved in 50 cc. of dioxane, the solution centrifuged, filtered, and the product precipitated by adding the dioxane solution dropwise to 500 cc. of dry ether. It was washed with ether, petroleum ether of b.p. 50–60° C. and finally with petroleum ether of b.p. 30–50° C. Yield, 7.0 gm. For analysis the product was dried at 110° C./2 mm. Found: OCH_3, 15.8%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3(OC_6H_5) . 3(C_6H_5OH)$, [1244.6] : OCH_3, 15.0%.

The product was repurified by the same procedure; OCH_3, 15.9%.

The phenol compound of Willstätter lignin premethylated with diazomethane is a light-brownish powder, and shows the same behavior towards solvents as the corresponding product obtained by direct phenolation of wood meal (2). The dioxane-ether solution is almost colorless. It was evaporated, the residual product dissolved in a very small amount of dioxane, and the solution added to ether. An additional small amount of the same phenolated compound separated out.

Acetylation of the product. Phenol lignin (0.5 gm.) from diazomethane-methylated Willstätter lignin was acetylated with pyridine and acetic anhydride. Yield, 0.6 gm. Found: OCH_3, 13.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCOCH_3)_3(OC_6H_5) . 3(C_6H_5OCOCH_3)$, [1496.7] : OCH_3, 12.5%.

Diazomethane-methylation of the Phenol Compound from Willstätter Lignin Premethylated with Diazomethane

A portion (5 gm.) of the phenol compound was methylated with diazomethane in dioxane solution in the usual manner, and the product purified. Found: OCH_3, 23.7, 23.6, 23.6%. Yield, 5 gm. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OH)_3(OC_6H_5)$. $3(C_6H_5OCH_3)$, [1300.6] : OCH_3, 23.8%. The product shows a behavior towards solvents similar to that of the product derived from the corresponding phenol lignin directly prepared from wood meal.

Acetylation of the product. A portion (1 gm.) of the above-mentioned diazomethane-methylated, phenol diazomethane-methylated Willstätter lignin was dissolved in 15 cc. of pyridine and 10 cc. of acetic anhydride. The solution was allowed to stand for 40 hr. at room temperature, then poured on to cracked ice, the precipitate filtered, washed with distilled water, and dried over sodium hydroxide and sulphuric acid. The crude acetyl derivative was dissolved in dioxane, filtered, and the product reprecipitated by adding the solution dropwise to dry ether. The light cream colored product was washed with ether, then several times with petroleum ether, and finally dried over sulphuric acid. Yield, 1.1 gm. Found: OCH_3, 21.6%. After another purification with dioxane and ether, the methoxyl content had not changed. Found: OCH_3, 21.8%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OCOCH_3)_3(OC_6H_5)$. $3(C_6H_5OCH_3)$, [1426.7] : OCH_3, 21.7%.

This product has the same properties as the corresponding derivative described previously, which had been prepared from phenol lignin obtained directly from wood meal.

Complete Methylation of the Diazomethane-methylated Phenol Lignin Prepared from Willstatter Lignin Premethylated with Diazomethane

A portion (1.5 gm.) of the phenol compound (OCH_3, 23.6%) was dissolved in 20 cc. of acetone and methylated with 20 cc. of dimethyl sulphate and 30 cc. of sodium hydroxide solution (30%), in the usual manner, at a temperature of 20–25° C. The acetone layer was separated from the aqueous solution, again methylated under the same conditions and a sample purified. Found: OCH_3, 29.7%. After a third methylation, the methoxyl content was 30.5%. After a fourth methylation the methoxyl value had not changed. Found: OCH_3, 30.4%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_{10}(OC_6H_5)$. $3(C_6H_5OCH_3)$, [1342.7] : OCH_3, 30.0%.

That the product was completely methylated was shown by treatment of a sample with acetic anhydride and pyridine, whereupon no change in the methoxyl content was found.

Methylation of Freudenberg Lignin with Diazomethane

The anhydrous Freudenberg lignin was isolated from its aqueous suspension in the same way as the Willstätter lignin. After complete removal of the water in the cyclohexanol suspension, diazomethane was introduced, causing a vigorous nitrogen evolution. After four methylations, using in each one

15 cc. of nitrosomethyl urethane, the methylated product was isolated in the same manner as that described for the Willstätter lignin. Found: OCH_3, 20.1%. After two further methylations the methoxyl content remained unchanged, and the cyclohexanol was then replaced by benzene and another methylation carried out. The benzene mixture of the reaction products remained colored for 24 hr., and the product was then treated in the same way as that described for Willstätter lignin. Found: OCH_3, 20.3, 20.2%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$ [886.4] : OCH_3, 21.0%.

Freudenberg lignin, methylated with diazomethane, is much lighter in color than the original Freudenberg lignin, but a little darker in color than the corresponding Willstätter lignin. It was free from nitrogen and insoluble in all solvents.

Preparation of the Phenol Compound of Freudenberg Lignin Premethylated with Diazomethane

Two grams of Freudenberg lignin premethylated with diazomethane (OCH_3, 20.2%) was suspended in 30 gm. of liquid phenol, and 1 cc. of ether containing 2.5% of hydrogen chloride introduced in the customary manner. The light-brown color changed immediately to dark purple, and on heating to 80° C. the mixture became increasingly viscous. After about 10 min. it was converted into a gelatinous mass. Another 1 cc. of the ether–hydrogen-chloride solution was then added. After about 30 to 40 min. the mixture became fluid again and most of the lignin had dissolved. The solution after heating for another hour was almost clear. The phenol was distilled off under reduced pressure, the dark reddish-brown syrupy residue was dissolved in 30–40 cc. of a mixture of equal parts acetone and methanol, centrifuged, and the clear solution poured into 500 cc. of distilled water. The phenolated lignin formed a colloidal solution and was flocculated out on addition of 1–2 cc. of sodium sulphate solution with stirring. It was filtered, washed with distilled water, and dried. Yield, 2.25 gm. OCH_3, 14.6%.

A second experiment with 4.5 gm. of Freudenberg lignin premethylated with diazomethane yielded 5.0 gm. of phenol compound. OCH_3, 14.4%.

The combined residues from the methyl alcohol-acetone solution were washed and dried. Weight, 0.25 gm., or 2.4% of the methylated lignin used. The crude phenolated compound (7.3 gm.) was purified by dissolving in 15 cc. of dioxane, centrifuging, filtering and precipitating by pouring into dry ether. The light cream colored product was washed with ether, then with petroleum ether and dried at 110° C./22 mm. Found: OCH_3, 15.1%. The methoxyl content did not change after a second purification. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_3(OC_6H_5)$. $3(C_6H_5OH)$, [1244.6] : OCH_3, 15.0%.

The dioxane-ether solution, on evaporation, left a small residue which was dissolved in dioxane and precipitated with ether. Yield, 0.15 gm. There was thus no dioxane-ether–soluble phenol product formed.

Acetylation of the product. A portion (0.5 gm.) of the phenol compound from diazomethane-methylated Freudenberg lignin was acetylated in the same manner as that described for the corresponding Willstätter lignin compound. Yield, 0.6 gm. Found: OCH_3, 12.3%. After another purification a methoxyl value of 12.4% was found. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCOCH_3)_3(OC_6H_5).3(C_6H_5OCOCH_3)$, [1496.7] : OCH_3, 12.5%.

Diazomethane-methylation of the Phenol Compound from Freudenberg Lignin Premethylated with Diazomethane.

The phenol compound (5 gm.) was methylated in dioxane solution in the usual manner with diazomethane until no further increase in the methoxyl content occurred. The product was purified and dried at 110° C./2 mm. Found: OCH_3, 22.8, 22.8%. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OH)_3(OC_6H_5).3(C_6H_5OCH_3)$, [1300.6] : OCH_3, 23.8%. Yield 5.0 gm.

Acetylation of the product. One gram of the last-named diazomethane-methylated phenol compound was acetylated in the same manner as that described for the corresponding Willstätter lignin compound. Yield, 1.1 gm. Found: OCH_3, 21.1%. No change in methoxyl value was found after a second purification. Calcd. for $C_{42}H_{31}O_5(OCH_3)_7(OCOCH_3)_3(OC_6H_5).3(C_6H_5OCH_3)$, [1426.7] : OCH_3, 21.7%.

Complete Methylation of the Diazomethane-methylated Phenol Compound from Freudenberg Lignin Premethylated with Diazomethane

The phenol compound (2 gm.) was methylated twice with dimethyl sulphate and sodium hydroxide according to the directions given for the corresponding Willstätter lignin compound. Found: OCH_3, 28.2%. No change in methoxyl value was found after a third methylation. Calcd. for $C_{42}H_{31}O_5(OCH_3)_{10}(OC_6H_5).3(C_6H_5OCH_3)$, [1342.7] : OCH_3, 30.0%.

After treatment with acetic anhydride and pyridine the methoxyl content was the same (28.3%), showing that the product had been completely methylated.

Action of Absolute Methanol and Hydrochloric Acid on Willstätter Lignin

Willstätter lignin was filtered from its aqueous suspension, washed several times with absolute methanol, and then shaken with the methanol and glass beads for several days with repeated renewal of the methanol. The lignin was then centrifuged, washed twice with anhydrous methanol and twice with highly purified dioxane. The lignin so prepared was suspended in a mixture of 50 cc. of pure anhydrous dioxane and 50 cc. of anhydrous methanol containing 2.5% of hydrogen chloride, and the product heated in a sealed tube for 16 hr. at 80° C. The light-brown lignin immediately turned dark violet, swelled, and acquired a flaky consistency. As the solution was only slightly colored, it was heated for a further eight hours at 110–125° C. Virtually complete solution of the lignin had occurred and the solution was dark brown. It was centrifuged, filtered, the solvents removed and the residue redissolved in anhydrous methanol containing a small amount of dioxane. The lignin was then precipitated as a buff colored product by adding the solution dropwise to distilled water. It was centrifuged, washed with water and dried at 110° C./2 mm. Found: OCH_3, 22.4%. There was no change on further purification. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$, [886.4] : OCH_3, 21.0%.

Action of Absolute Methanol and Hydrogen Chloride on Willstätter Lignin Premethylated with Diazomethane

Two grams of Willstätter lignin premethylated with diazomethane (OCH_3, 21.2%) was heated in a sealed tube with 200 cc. of anhydrous methanol containing 2% of hydrogen chloride. The light-yellow color of the lignin changed to reddish-brown. The mixture was then heated for 18 hr. at 70–80° C. but apparently no change took place. The temperature, therefore, was raised to 120° C. and the heating continued for 24 hr., whereupon a part of the lignin went into solution. It was heated for a further 72 hr. at the same temperature and the experiment interrupted after a total period of heating amounting to 125 hr. The solution was filtered from the insoluble material, concentrated under reduced pressure, and the lignin compound precipitated by pouring the solution into distilled water. The mixture was centrifuged, and the residue washed with distilled water and dried. Yield, 1 gm. The crude product was dissolved in dioxane and precipitated by addition of the solution to ether. The light-brown product was washed with fresh ether, twice with petroleum ether, and dried at 110° C./2 mm. Found: OCH_3, 24.4%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OH)_3$, [900.4] : OCH_3, 24.1%.

The brownish dioxane-ether solution was evaporated under reduced pressure, and the residual product dissolved in benzene. The solution was centrifuged, filtered, and the lignin compound isolated by adding the benzene solution dropwise to petroleum ether (60–70° C.). The precipitate was washed several times with petroleum ether and dried at 100° C./2 mm. Found: OCH_3, 25.7, 25.9%.

Complete Methylation of Willstätter Lignin Premethylated with Diazomethane

Four grams of Willstätter lignin premethylated with diazomethane (OCH_3, 21.2%) was methylated first in aqueous suspension with 25 cc. of dimethyl sulphate and 30 cc. of sodium hydroxide (30% solution). The latter methylations were carried out in acetone suspension with the same amounts of dimethyl sulphate and sodium hydroxide as employed previously. After the second methylation the methoxyl content was 32.8%, which did not change after two further methylations. The fully methylated lignin was filtered, washed consecutively with water, dilute acetic acid and dilute ammonium hydroxide solution, and finally boiled with distilled water for 15 min. The product was then filtered off, washed with boiling water and dried. A light cream colored powder resulted which was insoluble in all solvents. Found: OCH_3, 32.8%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_{10}$, [942.7] : OCH_3, 32.9%.

Complete Methylation of Freudenberg Lignin Premethylated with Diazomethane

Premethylated Freudenberg lignin (4 gm.; OCH_3, 20.2%) was suspended in 50 cc. of acetone and methylated with 50 cc. of dimethyl sulphate and 75 cc. of sodium hydroxide solution (30%). The reagents were added in the course of seven hours at 22° C. and the reaction mixture stirred for a further three hours. The methylated lignin was filtered off, washed with distilled water and acetone, and remethylated a second time. A sample was removed, washed with distilled water, dilute acetic acid, and water, and finally heated in boiling water for 15 min. It was filtered off and dried at 110° C./2 mm. Found: OCH_3, 30.3%.

After a further methylation the product was washed with distilled water, then with acetone, and finally heated in boiling water for 15 min. Found: OCH_3, 30.3%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_{10}$, [942.7] : OCH_3, 32.9%.

The fully methylated Freudenberg lignin is a fine, light-yellowish powder, the methoxyl content of which is not changed after treatment with pyridine and acetic anhydride. It is insoluble in all organic solvents.

Action of Methanol and Hydrochloric Acid on Freudenberg Lignin Premethylated with Diazomethane

Four grams of Freudenberg lignin premethylated with diazomethane (OCH_3, 20.2%) was heated in a sealed tube with 150 cc. of methyl alcohol containing 2% hydrogen chloride in a tilting oven for two days at 90–95° C., and for a further four days at 110–120° C. About 60% of the material went into solution. The product was isolated in the same way as that described for the corresponding Willstätter lignin. Yield, 2.1%. It was purified by dissolving the product in dioxane and precipitating it by adding the dioxane solution dropwise to dry ether. It could be separated into two portions, an ether-insoluble and an ether-soluble fraction. The purification was repeated. Yield of ether-insoluble product, 75%. Found: OCH_3, 22.7, 22.6%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OH)_3$, [900.4] : OCH_3, 24.1%.

The residue from the ether-dioxane mother liquor left after removal of the solvents was dissolved in a small amount of dioxane and the solution added dropwise to dry ether. The small precipitate was removed and the filtrate evaporated to dryness. The residue was dissolved in benzene and the product precipitated by adding the benzene solution dropwise to petroleum ether. Yield, 0.5 gm. The orange-colored product was then dried over alcohol. Found: OCH_3, 25.4, 25.5%.

Action of Methanol and Hydrogen Chloride on Fully Methylated Freudenberg Lignin

Fully methylated Freudenberg lignin (2.3 gm.; OCH_3, 30.3%) was suspended in a sealed tube in 200 cc. of absolute methanol containing 2% hydrogen chloride and heated in a tilting oven for 48 hr. at 78° C. and for 50 hr. at 105° C. The lignin went almost completely into solution. After cooling, the mixture was filtered and concentrated to about 75 cc., whereupon a part of the lignin product separated out. It was redissolved by addition of 25 cc. of acetone and the clear solution poured into a large volume of water. A colloidal solution was formed, and on addition of a few drops of concentrated sodium sulphate solution the product separated out as a flaky precipitate. It was filtered, washed with distilled water, and dried. Yield, 2 0 gm. The product was dissolved in dioxane and precipitated with ether, then washed with ether and petroleum ether, and dried over sulphuric acid. Found: OCH_3, 29.7%. After a second purification the methoxyl value was 29.6%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OH)$, [928.5] : OCH_3, 30.0%.

Action of Absolute Methanol and Hydrogen Chloride on Completely Methylated Spruce Wood Meal

Spruce wood meal (10 gm.) was methylated with dimethyl sulphate an sodium hydroxide first in aqueous and later in acetone suspension at room temperature to a final methoxyl content of 38.8%. A portion (4 gm.) of this material was mixed with 200 cc. of anhydrous methanol containing 2% of hydrogen chloride and then heated in a sealed tube at 80° C. for 48 hr., the tube being shaken throughout in the tilting furnace. The wood meal first turned red and then acquired a green color. That a part of the wood meal had dissolved was indicated by the brown color of the solution The tube was then heated at 105° C. for an additional 48 hr., when a further quantity of the wood meal had dissolved. After heating for another 15 hr. at 120° C. the greater part of the wood meal had dissolved. The mixture was filtered, the residue washed with methanol and dioxane, and finally with ether, and dried. Weight, 0.5 gm., or 20% of the wood meal used.

The methanol and dioxane solutions were united, concentrated, and the lignin precipitated by pouring the solutions into water. It formed a colloidal solution which could be coagulated by the addition of a trace of sodium sulphate.

The lignin was filtered, washed with distilled water and dried. OCH_3, 29.6%. Yield, 0.75 gm., or 26% of the methylated wood meal dissolved. This crude product was redissolved in 5 cc. of dioxane and reprecipitated with ether. It was isolated in the usual manner and dried at 100° C./2 mm. Yield, 0.4 gm. OCH_3, 28.6%.

The ether-dioxane solution, which was noticeably dark in color, was evaporated, the residual product dissolved in benzene, filtered and the product reprecipitated by pouring the solution into petroleum ether (60-70° C.). It was washed several times with petroleum ether and dried at 76° C./2 mm. Found: OCH_3, 29.5, 29.7%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_9(OH)$, [928.5]: OCH_3, 30.0%.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XVIII. LIGNIN SULPHONIC ACID—A PRELIMINARY INVESTIGATION ON ITS ISOLATION AND STRUCTURE[1]

By E. G. King[2], Fritz Brauns[3] and Harold Hibbert[4]

Abstract

Several methods for the isolation of a pure lignin sulphonic acid have been studied. A satisfactory method, employing dialysis in the presence of an excess of sulphurous acid, followed by precipitation with quinoline and subsequent decomposition with sodium hydroxide, has been developed. The free acid is unstable, becoming insoluble on standing or when heated above 50° C., particularly in the presence of mineral acids. Treatment with pyridine and acetic anhydride also yields an insoluble material. The salts of lignin sulphonic acid are stable towards heat and methylation reagents at room temperature, and therefore are more suitable for investigations on its structure. The methyl and benzyl esters have been prepared but in low yield only,—a result, presumably, of the well-known abnormally reactive character of esters of sulphonic acids. The permutoid character of its salts makes it difficult to prepare the neutral salts in a pure state. The pure sodium salt, however, was prepared by the use of electrometric titration to indicate the neutral point. The salts (Na, Tl, Ag) are soluble in alcohol containing a trace of water, but are precipitated by inorganic salts such as sodium or thallium acetate. The acid on methylation with methyl alcohol-hydrogen chloride yields a product which is soluble in organic solvents and in water, and which contains an additional methoxyl group. Methylation of the free acid with diazomethane gives a water-insoluble product (OCH_3, 18 4%), while a similar methylation of the sodium salt yields a water-soluble product (OCH_3, 19 4%, ash-free basis). The acid therefore contains at least one free phenolic or enolic hydroxyl group. It can be methylated at room temperature with dimethyl sulphate and sodium hydroxide (5% excess) to a maximum methoxyl content of 27 7% (ash-free basis), no structural change, other than the loss of some loosely bound sulphurous acid, apparently taking place. The analytical data provide additional support for the empirical formula for lignin proposed by Brauns and Hibbert.

Introduction

The solution of industrial problems such as the bleaching of pulp and the utilization of sulphite waste liquor is dependent to a large extent on a much more comprehensive knowledge of the structure and properties of lignin and, more specifically, of lignin sulphonic acid. A consideration, however, of the marked discrepancies in the results obtained by numerous investigators during the past 30 years indicates that very little definite progress has been made towards a final solution of the problem.

Accordingly it was considered advisable to investigate thoroughly the isolation, properties, and structure of lignin sulphonic acid. The first step is that of either adopting or developing a method for the isolation, without degradation, of a product free from inorganic salts and extraneous organic material.

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The isolation of lignin sulphonic acid has been carried out previously in three different ways, namely, by (*a*) precipitation, (*b*) salting-out, and (*c*) dialysis.

As precipitants, strong mineral acids (18), basic lead acetate (21), β-naphthylamine hydrochloride (11-16), quinoline (5), etc., have been used. Acids give only poor yields of a product that is difficult to wash and purify, while basic lead acetate precipitates phenolic compounds also. Dorée (2), however, claims to have separated sulphite waste liquor, after dialysis, into three fractions by use of the latter method.

Salts of the acid may be salted out of solution with calcium chloride or sodium chloride, etc. (17, 25, 26, 27). The yields (30–50%), however, are much poorer than those obtained by direct precipitation of an insoluble lignin sulphonic acid salt. Furthermore, the product is contaminated with large quantities of inorganic material, rendering a further purification necessary.

It is doubtful whether any of the methods previously used gives a product completely free from polysaccharides and other materials of high molecular weight, although the claim is made that this is accomplished after dialyzing for 14 days (8, p. 35-36). The yield by this method is about 66% of the total lignin contained in the liquor, which is considerably better than that obtained by other methods. However, as shown in the present investigation, the sodium lignin sulphonate thus obtained does not contain an equivalent amount of the sodium ion. Samec (29-31) prepared a lignin sulphonic acid directly from sulphite liquors by dialysis, and considered that his product was homogeneous since the barium salt could not be fractionated. It is possible that dialysis removes lignin-like materials of lower molecular weight, since it was observed in the present investigation that coloring matter was removed from the liquor during the earlier stages of the dialysis, in which parchment membranes were employed.

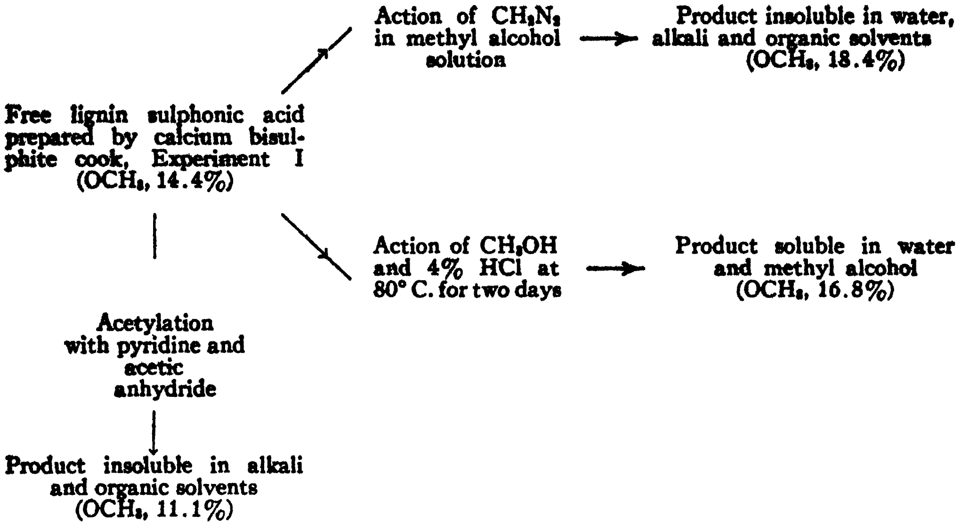
No satisfactory method for isolating lignin sulphonic acid in a pure state is therefore available, and in view of this a preliminary investigation of several methods was made.

The use of basic lead acetate was discarded when it was found impossible to wash the slimy precipitate free from carbohydrates without incurring large losses of the lead salt. Also, the barium and quinine salts were found to be of little use because of the experimental difficulties involved in handling and washing the product. Finally a modification of Freudenberg's method (7) (in which the product is precipitated with quinoline and isolated finally as the sodium salt) was adopted.

Action of Methylating and Acetylating Agents on Free Lignin Sulphonic Acid

The object of these experiments was to study the behavior of *free* lignin sulphonic acid towards common methylating and acetylating reagents, *e.g.*, diazomethane, methyl alcohol-hydrogen chloride, acetic anhydride and pyridine, with a view to determining the best reaction conditions. Chart I shows the nature of the results obtained. The behavior towards dimethyl sulphate is discussed in another section of this paper.

CHART I


Free lignin sulphonic acid prepared by calcium bisulphite cook, Experiment I (OCH_3, 14.4%)
Action of CH_2N_2 in methyl alcohol solution
Product insoluble in water, alkali and organic solvents (OCH_3, 18.4%)
Action of CH_3OH and 4% HCl at 80° C. for two days
Product soluble in water and methyl alcohol (OCH_3, 16.8%)
Acetylation with pyridine and acetic anhydride
Product insoluble in alkali and organic solvents (OCH_3, 11.1%)

The reaction products obtained from the free acid both on methylation with diazomethane and on acetylation with pyridine and acetic anhydride were insoluble not only in organic solvents, but also in hot sodium hydroxide and sodium ethylate. This may indicate that the sulphonic acid group had not been esterified and that some modification in structure, possibly involving this group, had taken place under the influence of these reagents.

The behavior of the free acid to these reagents demonstrates the extreme sensitiveness and instability of this product. From later work it was found that the solid sodium salt was much more stable than the free acid both towards heat and on standing, and it therefore served as a valuable material for further investigation. Diazomethane is an exceedingly reactive agent, while the esters of sulphonic acids also have shown a somewhat abnormal activity, so that a methyl ester of lignin sulphonic acid might also be expected to show a readiness to undergo inter- and intra-molecular changes.

The product obtained by heating the *free* lignin sulphonic acid (OCH_3, 14.3%) with absolute methyl alcohol and 4% hydrogen chloride contained 16.8% methoxyl*, indicating that this product possessed one more methoxyl group than the original acid (see Table I). It is of interest that this product was apparently more stable than the original material.

Isolation of Salts and Esters of Lignin Sulphonic Acid

From these results it appeared that esters, or neutral salts, of lignin sulphonic acid would be more suitable products for investigations dealing with chemical structure.

**These values all refer to ash-free products (see Table I).*

Previous preparations of metallic salts of lignin sulphonic acid, *e.g.*, barium salts (17, 18, 24), were undoubtedly contaminated with inorganic matter such as barium carbonate, hydroxide or sulphate.

Attempts by the authors to prepare a neutral thallium salt were also unsatisfactory for the same reason.

Preparation of esters. It is evident that the isolation of a derivative soluble in organic solvents such as benzene or dioxane would eliminate this objection and possibly provide, at the same time, a means of purification from other impurities. The esters of lignin sulphonic acid, it was thought, would satisfy these conditions, but attempts to prepare the pure methyl and benzyl esters of the diazomethane-methylated lignin sulphonic acid were not very satisfactory (yields, 10–20%). The products, however, were soluble in organic solvents, the methyl and the benzyl esters containing 22.0% and 18.1% OCH_3 respectively.

The residues left after extraction of the esters with organic solvents were no longer soluble in water and alkali—an indication that some fundamental change had occurred in the molecule, presumably a result of either an intramolecular reaction involving the sulphonic acid group or a secondary intermolecular change involving the reactive ester. This change is apparently similar to that observed when the free acid is methylated with diazomethane.

Esters of sulphonic acids are very reactive substances that can be used as alkylating agents where dimethyl sulphate and alkali cannot be employed, for example, with phenolic aldehydes (28). They are used also to introduce both aryl and alkyl groups into the nucleus or side chains of a benzene ring. Földi (5) has shown that toluene sulphonic acid ethyl ester reacts with benzene to give mono-, di- and triethyl benzenes, while benzene sulphonic acid benzyl ester reacts with benzene yielding a mixture containing diphenyl methane and dibenzyl benzene. The benzyl ester is very reactive and attacks the nucleus (4). This reactivity of the sulphonic esters may be expected to become still more pronounced in the presence of the more reactive lignin molecule.

Preparation of a neutral sodium lignin sulphonate. The attempts to prepare a pure sodium salt by precipitation from a slightly acid solution by means of absolute ethyl alcohol were unsuccessful, because the presence of the acid (hydrochloric) brought about a partial replacement of the sodium by hydrogen, a consequence of the permutoid character of the lignin sulphonic acid (19). In view of the greater solubility of sodium acetate in alcohol and the weaker character of acetic acid, the latter was substituted later for the hydrochloric acid, and sodium lignin sulphonate containing 5.16% sulphur and 4.05% sodium was obtained. The latter value is slightly higher than that of the neutral sodium salt prepared by electrometric titration (Na, 3.7%) as described below.

Two dialysis experiments, using a parchment bag, were carried out with the sodium lignin sulphonate. It was found that for a definite pH value the product contained a definite amount of metallic ion. Thus for pH values of 7 and 4 the sodium contents were 4.2% and 2.5% respectively. After long-continued dialysis, the sodium salt, prepared from the commercial bisulphite liquors, always retained the same amount of sodium (2.4 to 2.5%), indicating that a definite equilibrium was finally established in the dialysis process. As shown later, the latter value for the sodium content is less than that required for the formation of a neutral sodium lignin sulphonate, so that the latter cannot be prepared by dialysis alone. However, the method is of importance since it may be used to prepare a lignin sulphonate in which all the sodium present is combined with the sulphonic acid group, thus permitting an accurate calculation to be made on an ash-free basis.

The neutral sodium salt of lignin sulphonic acid may be prepared by neutralization, the endpoint being determined potentiometrically. The neutral sodium lignin sulphonate was found to have a pH value of 6, and a sodium content of 3.7%, the latter value being equivalent to the actual sulphur content (5.36%) calculated on an ash-free basis. A portion of the sulphur is held in a loosely bound state since, as is subsequently shown, it is split off during the methylation with dimethyl sulphate and alkali.

Methylation of Sodium Lignin Sulphonate with Diazomethane

Using the sodium salt of lignin sulphonic acid (OCH_3, about 13.2%), a product fully methylated with respect to diazomethane was obtained, without the formation of any insoluble by-product such as that obtained when the free acid is methylated with the same reagent. The resulting cream-colored product (OCH_3, 19.4%) was soluble in methyl alcohol and in water.

Methylation of Lignin Sulphonic Acid with Dimethyl Sulphate in Alkaline Solution

The methylation of lignin sulphonic acid with dimethyl sulphate has been attempted by several investigators (10; 13; 8, p. 85; 27) but with little success, the end product being generally an insoluble material of lower sulphur content than the original substance and possessing a methoxyl value considerably lower than that obtained in the present investigation. Hägglund (9), on the other hand, methylated several lignin sulphonic acids isolated from commercial waste liquors and obtained a final average methoxyl content of 30.8%, while with lignin sulphonic acids prepared from various isolated lignins (Freudenberg and Willstätter lignins) a methylated product with a methoxyl content of 32% was obtained. Such results need occasion no surprise since, as will be shown in a later communication, when lignin derivatives, *e.g.*, methyl alcohol lignin, are treated with 40% alkali at room temperature structural changes apparently occur with the possible formation of new hydroxyl groups.

Freudenberg (7) in 1933 obtained a maximum value of 27.7% methoxyl for the free acid, but gave no details of his technique.

By studying the behavior of the lignin sulphonic acid during methylation, the most suitable and efficient conditions for complete methylation were determined, and are given in the Experimental Part. The product was fully methylated after five methylations (OCH_3, 26.5%). Calculated on an ash-free basis, the value (27.7%) agrees very well with that observed by Freudenberg (7).

Theoretical Considerations

Although the true mechanism of sulphonation is not as yet understood, and the problem of the structure of lignin sulphonic acid requires further extended and intensive investigation, it is possible, with the present results, to make some interesting speculations involving the lignin "building unit", $C_{47}H_{52}O_{16}$, proposed by Brauns and Hibbert (1).

It is apparent, from a review of the various theories concerning the mechanism of the process of sulphonation, that there are two ways in which formation of a stable sulphonic acid may take place without involving the formation of a new hydroxyl group; namely, (*a*) by addition of sulphurous acid to an ethylenic linkage, and (*b*) by sulphonation of an aromatic nucleus. The formula for a lignin sulphonic acid derived from the "building unit" of Brauns and Hibbert and containing the *same number of hydroxyl groups* would be

$$C_{42}H_{32}O_6(OCH_3)_5(OH)_5HSO_2OH \qquad (I)$$

Freudenberg (6, p. 128) has stated that it is possible that the sulphurous acid adds to a double bond, formed by the loss of a molecule of water. Another theory, also mentioned by Freudenberg (6, p. 128), is the possibility of the direct sulphonation of an aromatic nucleus. A more recent and important investigation on the action of bisulphites on resorcinol (20) tends to support this view and shows that such a sulphonation is accompanied by the loss of one hydroxyl group.

On the basis of the above "building unit" of Brauns and Hibbert the corresponding formula for both of the above cases in which *one hydroxyl group disappears* would be

$$C_{42}H_{31}O_6(OCH_3)_5(OH)_4HSO_2OH \qquad (II)$$

In Table I a comparison is made of the methoxyl values found for the various derivatives prepared in the present investigation with those calculated from the above formulas.

The experimental value for the methoxyl content of the free lignin sulphonic acid (14.4%) lies between the calculated values for the two formulas (I and II) containing four and five methoxyl groups respectively. This fact may be due to a loss of methoxyl groups during the sulphite cooking process.

Although the calculated values for these formulas agree very well with those found experimentally, further investigation is necessary before a final decision can be made as to the true "building unit" of lignin sulphonic acid. However, the value of the fully methylated acid (27.7%, Table I) lends some support to the theory that the formation of the lignin sulphonic acid is preceded by the removal of a molecule of water.

Experimental

Experiment I—Preparation and Isolation of Lignin Sulphonic Acid (Laboratory Cook)

Resin-free and vacuum-dried wood meal (588 gm., 65 mesh) was heated with 10 litres of calcium bisulphite liquor (containing 1 gm. of CaO and 4 gm. of SO_2 per 100 cc. water) in a chrome-nickel autoclave for two hours at

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED METHOXYL VALUES OF LIGNIN SULPHONIC ACID DERIVATIVES*

Description of product	Methoxyl content		
	Found %	Calcd. for Formula I $C_{42}H_{32}O_6(OH)_5(OCH_3)_5HSO_2OH$ (m.w. 954), %	Calcd. for Formula II $C_{42}H_{31}O_6(OH)_4(OCH_3)_5HSO_2OH$ (m.w. 936), %
Free lignin sulphonic acid (*M*) prepared by the action of calcium bisulphite (Exp. I)	14 4	For 4 OCH_3, 13.2 For 5 OCH_3, 16.2	For 4 OCH_3, 13.4 For 5 OCH_3, 16.6
Lignin sulphonic acid (*N*) isolated as the sodium salt from commercial waste sulphite liquor	14 2	For 4 OCH_3, 13.2 For 5 OCH_3, 16 2	For 4 OCH_3, 13.4 For 5 OCH_3, 16.6
Acetylated lignin sulphonic acid from (*M*)	11.1	11.4	11.7
Lignin sulphonic acid from (*M*) methylated with methyl alcohol-hydrogen chloride	16 8	17.3	17.4
Sodium salt of lignin sulphonic acid from (*N*) methylated with diazomethane	19.4	For 6 OCH_3, 19.2	For 6 OCH_3, 19.6
Esters of lignin sulphonic acid from (*N*) previously methylated with diazomethane			
(*a*) Benzyl ester	18 0	For 6 OCH_3, 17 6	For 6 OCH_3, 17.7
(*b*) Methyl ester	22 0	For 7 OCH_3, 22.1	For 7 OCH_3, 22.5
Fully methylated lignin sulphonic acid from (*N*)	27 7	For 9 OCH_3, 27.6 For 10 OCH_3, 30.8	For 9 OCH_3, 28.1

Results calculated on an ash-free basis.

100–110° C., followed by a further 4.5 hours at 122° C. The light-brown wood meal was filtered and the filtrate, together with the washings, concentrated under reduced pressure at 30° C. to about two litres, and the calcium removed by precipitation with sodium carbonate. The filtrate was acidified with sulphuric acid (20%) until the change in color from brown to yellow occurred, then concentrated under reduced pressure, the temperature being kept below 40° C., and dialyzed for two days in a parchment bag with running distilled water.

The dialyzed solution was filtered through a thin layer of charcoal, the lignin sulphonic acid precipitated as the lead salt by addition of a hot concentrated solution of lead acetate, and the mixture centrifuged. The mother liquor was again treated with lead acetate and a few drops of ammonium hydroxide, whereupon a further quantity of the lead salt was thrown down, complete precipitation having presumably been prevented by the presence of acetic acid. It is therefore advisable to use a solution of *basic* lead acetate. The combined precipitates were washed with hot water and treated with 5% sulphuric acid in slight excess. The brown solution was filtered through charcoal, and the lignin sulphonic acid reprecipitated as the lead salt with basic lead acetate. The gelatinous, gummy material was washed by stirring the product with water and centrifuging. The product, which had been washed with about eighteen litres of distilled water, reduced Fehling's solution only very slightly. The free acid was again liberated with slight excess of sulphuric acid and the solution, after filtration through charcoal, dialyzed in a parchment bag.

The solution, which had increased considerably in volume, was concentrated under reduced pressure below 40° C. A precipitate separated out. This occurred more readily when the sulphuric acid had not been completely removed by dialysis. The concentrated solution was electrodialyzed continuously for one week, filtered, concentrated at 25–30° C. to a very thick syrup and extracted with absolute methyl alcohol. The dissolved, free lignin sulphonic acid was precipitated as a coarse gray powder by pouring the methyl alcohol solution with rapid stirring into dry ether. It was filtered off, washed with ether, then with petroleum ether, and dried in a vacuum desiccator over sulphuric acid. Found: OCH_3, 14.1; ash, 1.63%. Calcd. on an ash-free basis for the free acid: OCH_3, 14.4%.

Experiment II—Isolation of Lignin Sulphonic Acid from Commercial Calcium Bisulphite Liquor

The calcium bisulphite waste liquor used was taken from a commercial digester of the Howard Smith Paper Mills, prior to increasing the temperature above 125° C., and, therefore, before the darkening in color had occurred. The calcium was precipitated with excess sodium carbonate and the filtrate concentrated under reduced pressure, at a temperature not above 25° C., to a thick viscous syrup. It was then dialyzed in a parchment bag with running distilled water, sulphur dioxide meanwhile being passed into the solution. After six days the dialysis was complete, the liquor being almost free from reducing sugars and inorganic salts. The volume was made up to five litres, the solution acidified (Congo paper) with dilute sulphuric acid, and the lignin sulphonic acid precipitated by addition of a concentrated solution of quinoline sulphate. The cream-colored, curdy quinoline salt was allowed to settle, and the supernatant liquor removed. The precipitate was washed with dilute quinoline sulphate and centrifuged. It was then decomposed with dilute sodium hydroxide, reprecipitated with acidified quinoline sulphate and washed with dilute quinoline sulphate. The precipitate was decomposed with an excess of dilute sodium hydroxide (5%), the solution concentrated at 30° C. under reduced pressure and extracted for 48 hr. with ether to remove the quinoline. The aqueous solution was acidified with dilute sulphuric acid (10%) and extracted a further 48 hr. with ether. The concentrated aqueous solution was then dialyzed in a parchment bag for several days, the solution being concentrated when found necessary.

The product is an equilibrium mixture of the free lignin sulphonic acid and the sodium salt of lignin sulphonic acid and is completely free from inorganic matter, carbohydrates, tannins and other resinous material. The free acid was prepared by a long-continued electrodialysis of this solution with frequent additions of sulphuric acid. However, since it was found that the sulphonic acid is unstable, the material was converted into the sodium salt and retained in the form of a stable aqueous solution for subsequent use.

Behavior of Free Lignin Sulphonic Acid towards Methylating and Acetylating Agents

The following experiments were carried out with the free lignin sulphonic acid (OCH_3, 14.4%) prepared in Experiment I.

(*a*) *Behavior towards diazomethane.* Lignin sulphonic acid (0.5 gm.), dissolved in absolute methyl alcohol, was methylated with diazomethane obtained from 2 cc. of nitroso-methyl urethane. During the reaction the product separated out as a brown flocculent precipitate from the pale amber-colored solution. It was allowed to stand overnight and, after washing it with methyl alcohol, ether and petroleum ether, it was dried in a vacuum desiccator over sulphuric acid. The yellowish-brown product was insoluble in hot and cold aqueous and alcoholic sodium hydroxide, as well as in common organic solvents. It contained no nitrogen. Found: Ash, 0.05%; OCH_3, 18.4%.

(*b*) *Acetylation with pyridine and acetic anhydride.* Methyl-alcohol soluble lignin sulphonic acid (OCH_3, 14.4%; 0.3 gm.) was added to a mixture of 10 cc. of pyridine and 5 cc. of acetic anhydride. The lignin sulphonic acid suspension became, almost immediately, flocculent in appearance and lighter in color. The mixture was shaken 24 hr. and then poured on to 400 cc. of cracked ice. The suspension was centrifuged and the product washed and dried. The dark, horny material, which was insoluble in sodium hydroxide and organic solvents, was powdered in an agate mortar and dried. Found: Ash, 0.66; OCH_3, 11.0%. Corrected OCH_3 for the ash-free acid, 11.1% (Table I).

(*c*) *Action of methyl alcohol containing anhydrous hydrochloric acid.* The lignin sulphonic acid (OCH_3, 14.4%) used in this experiment had become partially insoluble in absolute methyl alcohol. A suspension of 0.2 gm. in 25 cc. of methyl alcohol containing 4% anhydrous hydrochloric acid was heated in a sealed tube, with shaking, at 80° C., for two days. A small insoluble residue remained. The filtrate was concentrated at room temperature and the reaction product precipitated by pouring into ether. Yield, 80%. Found: Ash, 3.11; OCH_3, 16.3%. Corrected OCH_3 for the ash-free acid, 16.8% (Table I).

Preparation of the Methyl Ester of Lignin Sulphonic Acid Premethylated with Diazomethane

A methyl alcohol solution of the sodium salt of lignin sulphonic acid (0.5 gm.) which had been previously methylated with diazomethane to a methoxyl content of 18.4% was added to a solution of 0.16 gm. of silver nitrate in 75 cc. of methyl alcohol. About 0.5 gm. of the freshly precipitated silver salt thus obtained was suspended in dioxane and heated with 4 cc. of methyl iodide under pressure for 12 hr. at 80° C. The dioxane solution after centrifuging was concentrated to about 10 cc., filtered, and precipitated in ether. The grayish-fawn colored material obtained after washing with ether and petroleum ether, and drying, was soluble in the common organic solvents. Yield, 0.05 gm. Found: OCH_3, 22.0% (Table I). The residue was insoluble in the same solvents and in water.

Preparation of the Benzyl Ester of Lignin Sulphonic Acid Premethylated with Diazomethane.

The dry silver salt of diazomethane-methylated lignin sulphonic acid (0.5 gm.) was suspended in 20 cc. of dioxane and heated with 1 cc. of freshly distilled benzyl chloride (b.p. 176° C.) at 70–80° C. for five hours. As no appreciable change in the reaction mixture was observable it was heated for a further four hours at 100° C. The reaction was carried out with stirring, in the absence of moisture, in a glass apparatus with a mercury seal. The suspension was centrifuged, the residue washed with dioxane, and the combined mother liquor and washings concentrated under reduced pressure to a small volume. The product was precipitated in ether, washed and dried in the usual manner. Yield, 0.12 gm. Found: OCH_3, 18.1% (Table I).

Preparation of the Sodium Salt of Lignin Sulphonic Acid

Method 1.—Precipitation from ethyl alcohol solution. Purified lignin sulphonic acid, prepared from commercial bisulphite liquor (Experiment II) and containing some sodium bicarbonate, was concentrated to a thin syrup. It was then made slightly acid with hydrochloric acid, filtered, and added dropwise to 15 times its volume of absolute ethyl alcohol. The slimy precipitate was washed with absolute alcohol—a matter of considerable difficulty owing to the formation of heavy suspensions. A small sample was washed further with ether and petroleum ether and dried. Found: Na, 3.12, 3.16; OCH_3, 13.7%. Corrected OCH_3 for the ash-free acid, 14.1%.

The continued repetition of this procedure yielded a product with a sodium content of 1%, indicating that the hydrochloric acid merely removed sodium and liberated the free acid.

Method 2.—Precipitation with alcohol from a solution containing a slight excess of sodium acetate. A concentrated solution of the dialyzed lignin sulphonic acid (3 gm.) obtained from commercial waste sulphite liquor (Experiment II) was acidified with acetic acid, and the material precipitated in a litre of absolute ethyl alcohol. The flocculent precipitate was centrifuged and washed twice with absolute alcohol. A sample was washed carefully with ether, the product being allowed, during each washing, to stand in contact with the ether for some time, then treated similarly with petroleum ether, and the light grayish-brown fluffy product dried at 100° C. and 12 mm. pressure over phosphorus pentoxide. Found: Na, 4.12, 3.97; S, 5.12, 5.19%. Corrected for the ash-free acid: S, 5.36%.

Method 3.—By dialysis. In order to investigate dialysis as a method for the preparation of the neutral sodium salt of lignin sulphonic acid, the following experiments were carried out: (*a*) determination of the sodium content of the sodium salt of lignin sulphonic acid prepared by dialyzing to a pH of 7; (*b*) dialysis of the sodium salt to a constant sodium content.

Experiment (*a*): A sample of the pure lignin sulphonic acid (Experiment II) containing an excess of sodium bicarbonate was placed in a small parchment bag and dialyzed. The results are summarized in Table II.

TABLE II

VARIATION IN SODIUM CONTENT OF THE SODIUM LIGNIN SULPHONATE SOLUTION WITH pH VALUE BETWEEN 6 AND 7

Progressive treatment of sodium salt of lignin sulphonic acid	Sodium, %	pH of solution*
Dialyzed 24 hr., 1 cc. NaOH (30%) added, and dialyzed a further 20 hr.	4.0	6.3 to 6.4
1 cc. NaOH (30%) added, dialyzed 18 hr., sufficient NaOH (6%) added to give a pH of 7 and one drop in excess	4.37	Above 9
Dialyzed a further 18 hr.	3.82	5.9 to 6.0
Sufficient NaOH (1%) added to give a pH of 7	4.22	7.0 to 7.1

**The pH measurements were made using the Wulff "Indikator-Folien" method.*

Experiment (*b*): A sample of the same sodium lignin sulphonate solution as used in Experiment (*a*) was dialyzed continuously in a small parchment bag without any addition of sodium hydroxide. An aliquot portion was taken at intervals to determine the sodium content of the solid material and the pH of the solution. Constant values of 2.41% for sodium and 4 to 4.2 for pH were obtained after six to seven days' dialysis. The solution was acidified with acetic acid and dialyzed for 24 hr. The sodium content was then found to be 1.31%, indicating the ease with which the equilibrium is disturbed. About 0.5 gm. of sodium acetate was added and the solution again dialyzed until the sodium content was constant (2.49%). A solution of the sodium lignin sulphonate, therefore, can be dialyzed to a constant sodium content (2.4 to 2.5%), which is less than the amount of sodium equivalent to the sulphur content of the lignin sulphonic acid.

Method 4.—Electrometric titration: The most satisfactory method for preparing a neutral sodium lignin sulphonate is by the use of electrometric titration to the point of neutrality.

The potentiometric titration was carried out using the circuit and set-up of MacInnes (22, 23) and of Elder (3)*. The glass electrode was first standardized by means of two buffer solutions of known pH, 3.5 and 5.5 respectively.

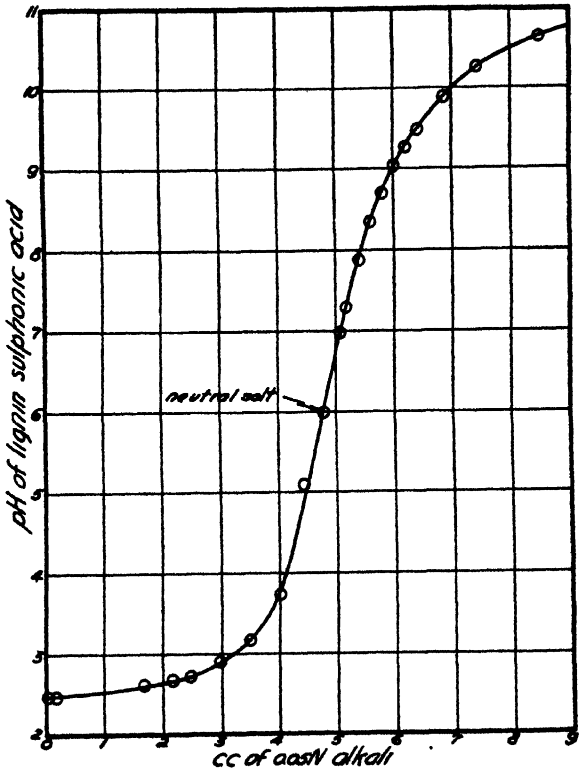


FIG. 1. *Electrometric titration curve of lignin sulphonic acid.*

The potential of the cell, formed by combination of the buffer solution with a calomel half-cell and a hydrogen electrode, was measured in each case with a Leeds and Northrup potentiometer, and amounted to 0.166 and 0.274 volts

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respectively. The potentiometer readings were plotted on a graph against the corresponding pH values of the buffers. The straight line graph obtained by joining these two points gave the variation of the potentiometer reading with the pH value. The two half-cells were connected by means of 50 cc. of lignin sulphonic acid solution (containing about 1.7% sodium based on the anhydrous weight of the lignin sulphonic acid present). The potentiometer readings corresponding to the additions of small volumes of standardized 0.05 *N* sodium hydroxide to the lignin sulphonic acid solution were observed, and the corresponding pH values obtained from the curve. These values were plotted, using the pH values as ordinates and the number of cubic centimetres of 0.05 *N* alkali as abscissas (Fig. 1). The midpoint between the two breaks (pH, 7.85 and 4.15) in the curve was taken as the endpoint of the reaction, this corresponding to a pH value of 6 (equivalent to the addition of 4.85 cc. of 0.05 *N* sodium hydroxide).

A second 50 cc. of the same lignin sulphonic acid solution was then neutralized with 4.85 cc. of the sodium hydroxide solution previously employed, the sodium content of the sodium lignin sulphonate determined and found to correspond to that obtained for the sodium salt prepared by Method 2. Found: Na, 3.71; S, 5.1%.

The product is therefore the true *neutral* sodium salt of lignin sulphonic acid, since the stoichiometric ratio of sodium to sulphur (23 : 32 or 1 : 1.4) is that actually found for the sodium salt (3.7 : 5.1 or 1 : 1.4). The discrepancy between the found and calculated values arises from the presence in the sodium product of some sodium salt of a higher sulphonated unstable acid in addition to the sodium monosulphonate. Calcd. for $C_{42}H_{31}O_6(OH)_4(OCH_3)_5H.SO_2ONa$: Na, 2.4; S, 3.3%.

Methylation of the Purified Sodium Salt of Lignin Sulphonic Acid with Diazomethane

To show that a methylation of the phenolic hydroxyl group may be carried out without a simultaneous esterification of the —SO_3H group, a sample of the sodium salt of 1 : 4 α-naphthol sulphonic acid was methylated in absolute methyl alcohol solution with diazomethane. Found: OCH_3, 11.7%. Calcd. for $C_{11}H_9O_4SNa$: OCH_3, 11.9%.

Pure sodium lignin sulphonate was then methylated several times in the following manner. Diazomethane from 15 cc. of nitroso-methyl urethane was passed into a concentrated aqueous solution of the purified sodium salt of lignin sulphonic acid (OCH_3 about 13.2%) cooled in an ice bath. The mixture was allowed to stand for 24 hr. at 16° C. An aliquot portion was then filtered and the product precipitated by adding the solution to a mixture of 70 parts of alcohol and 30 parts of ether. The light cream colored product was washed successively with alcohol-ether, ether-petroleum ether and petroleum ether, and dried over sulphuric acid in a vacuum desiccator. A sample was dried at 100° C. for 12 hr. under reduced pressure and analyzed for methoxyl content. The main portion of the solution was methylated in this manner to constant methoxyl content, using different solvents. During the latter methylations a violent evolution of nitrogen occurred and the solution became much lighter in color. The results are shown in Table III.

TABLE III

METHYLATION OF SODIUM LIGNIN SULPHONATE WITH DIAZOMETHANE

Description	Methoxyl content, %
Sodium lignin sulphonate	13 2
After first methylation (in aqueous solution)	14.6
After second methylation (in aqueous solution)	14.9
After third methylation (in aqueous acetone)	16.0
After fourth methylation (in 98% acetone)	17.3
After fifth methylation (in methyl alcohol)	18 4
After sixth methylation (in methyl alcohol)	18.4

The final product, containing an excess of sodium bicarbonate, was dialyzed for three days with the addition of acetic acid and isolated by the usual procedure. Found: OCH_3, 18 9, 18.8; Na, 3.00%. Corrected OCH_3 for the ash-free product: 19.4%.

Methylation of the Sodium Salt of Lignin Sulphonic Acid with Dimethyl Sulphate

The sodium salt (10 gm.) prepared from commercial sulphite liquor (Experiment II) was dissolved in the least possible amount of water and 100-150 cc. of acetone added. The methylation was carried out in homogeneous phase at 25° C., five consecutive additions being made over a period of five hours. Each addition occupied 20 min., during which period a simultaneous addition of 24 cc. of dimethyl sulphate and 38 cc. of 30% sodium hydroxide was made, and the stirring continued for a further 40 min. The mixture, after having been stirred for a further two hours to complete the reaction, was slightly alkaline. Any salting-out of the material during the process indicated too high a concentration of alkali and was adjusted either by the addition of more acetone to the reaction mixture or by an increase in the rate of flow of the dimethyl sulphate.

The amber-colored solution was dialyzed overnight with distilled water. The liquid, which had then almost doubled in volume, was concentrated to about 500 cc. under reduced pressure at 30-35° C. in a "foam-breaker" distillation flask. It was then dialyzed for about 36 hr. until presumably free from sulphate. The solution was concentrated to about 100 to 150 cc. and methylated four times in the same manner. The final solution was dialyzed for 54 hr. and a small sample concentrated to dryness. The product was dissolved in methyl alcohol and precipitated in 10 times its volume of ether. The fine, canary-yellow colored precipitate was washed consecutively with alcohol, ether and petroleum ether, and dried.

The remainder was methylated for a fifth and sixth time by the same technique, the solution dialyzed for 54 hr. in distilled water, and a sample analyzed. The results are contained in Table IV.

TABLE IV

METHYLATION OF SODIUM LIGNIN SULPHONATE WITH DIMETHYL SULPHATE

Description	Na %	OCH_3 %
Sodium lignin sulphonate	—	13.2
After fourth methylation	3.49	26.2
After fifth methylation	3.34	27.0
After sixth methylation	3.37	26.5

Calculated on an ash-free basis, the fully methylated lignin sulphonic acid contained 27.7% OCH_3.

A solution of the fully methylated lignin sulphonic acid was electrodialyzed. Found: Na, 0.89; S, 3.08, 3.15%. Corrected sulphur content for the ash-free product: 3.15%.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XIX. ALKALI LIGNIN[1]

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Abstract

Alkali lignin was prepared by the method of Mehta (6). It was separated into two fractions, termed Alkali Lignin A, insoluble in dioxane-ether, and Alkali Lignin B, soluble in dioxane-ether. Both compounds were acetylated, partially methylated with diazomethane and fully methylated using dimethyl sulphate and sodium hydroxide. Treatment of both alkali lignins with phenol, using hydrogen chloride as catalyst, yielded phenol condensation products. Phenol Alkali Lignin A was acetylated, partially methylated with diazomethane and completely methylated with dimethyl sulphate and sodium hydroxide. It was found that one mole of Alkali Lignin A reacted with two moles of phenol. Alkali Lignin B yielded two phenol derivatives, an ether-insoluble and an ether-soluble product, which differ in the number of attached phenol groups. *p*-Bromphenol and *o*-bromphenol were also shown to react with Alkali Lignin A giving lignin derivatives having identical methoxyl and bromine content. On treatment of Alkali Lignin A with anhydrous methyl alcohol and hydrogen chloride a product with a higher methoxyl content was obtained, indicating the presence of hydroxyl groups capable of methylation with this reagent. From the analytical data of the different compounds some theoretical conclusions are drawn, and empirical formulas derived.

Introduction

Alkali lignin, that is, lignin isolated with alkali and precipitated by means of mineral acids, has been used as a starting material by many investigators. The results obtained, however, varied so remarkably that it was necessary to re-investigate the subject by carrying out the extraction of the lignin under certain well defined conditions. The alkali lignin so obtained could be separated into a dioxane-ether insoluble fraction (Alkali Lignin A) and a dioxane-ether soluble fraction (Alkali Lignin B). Alkali Lignin A has a methoxyl content of 15.0%, which differs markedly from that obtained by other investigators (4, 6). Alkali Lignin B has not been isolated hitherto by any investigator, in spite of the fact that it is present in an appreciable quantity (20%). Its methoxyl content (14.0%) is only a little lower than that of Alkali Lignin A, but a more striking difference between them is found in their behavior on methylation.

From both alkali lignins, acetylated, partially methylated and fully methylated derivatives were prepared, thus indicating that they contain free hydroxyl groups. Methylation with diazomethane gives products of a higher methoxyl value which still contain free hydroxyl groups, as shown by acetylation and by complete methylation with dimethyl sulphate and sodium hydroxide. Since the methoxyl groups are stable towards alcoholic sodium hydroxide solution, the absence of carboxyl groups is indicated.

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Treatment of Alkali Lignin A with methyl alcohol and hydrogen chloride increases the methoxyl content by 5.4%, and a subsequent treatment with diazomethane caused an additional increase of about 8%.

The action of phenol on Alkali Lignin A yields a condensation product and since in three different experiments a product with the same methoxyl value was always obtained, it seems that the phenol and Alkali Lignin A react in a definite stoichiometrical proportion. Acetylation, partial and complete methylation of Phenol Alkali Lignin A was carried out in order to determine the number and type of the free hydroxyl groups.

Treatment of Alkali Lignin A with *p*- and *o*-bromphenol gives condensation products having the same methoxyl (13.5%) and bromine content (6 05%). These bromphenol compounds may be used as a basis for the theoretical considerations of the experimental results.

The bromine content of *p*-bromphenol (m w. = 173) is 46 2%, while that of both phenol lignins is 6 05%. From these figures a value for the molecular weight, M, of the *p*-Bromphenol Alkali Lignin A building unit may be calculated by use of the following equation, in which the amount of bromine present in each compound is equated:

$$\frac{6\ 05}{100} \times M = \frac{46\ 2}{100} \times 173,$$

or

$$M = 1321.$$

This value represents the smallest molecular weight for the Bromphenol Alkali Lignin A building unit, in which only one bromphenol has reacted with each lignin unit Evidence for the correctness of this value is shown by the agreement between the methoxyl values of the different Alkali Lignin A derivatives found experimentally, and those calculated on the basis of this molecular weight.

It is obvious that this value cannot be regarded as accurate within narrow limits, as a small error in bromine or methoxyl content causes an appreciable difference in the resulting molecular weight. These differences, however, are still within the error allowable in molecular weight determinations.

Three combustions of Alkali Lignin A gave the following average values:— carbon, 64.75; hydrogen, 5.71; oxygen, 29.54%. The methoxyl content was 15.0%. From these values the following empirical formula is obtained:

$$C_{5.39}H_{5.66}O_{1.84} \text{ and } (OCH_3)_{0.48}$$

Since each Alkali Lignin A unit must possess a definite whole number of methoxyl groups, the molecular weight of this unit can be calculated from the methoxyl content and the number of methoxyl groups present. If it be assumed that each unit contains only one methoxyl group, then the molecular weight, *M*, of the smallest unit can be calculated as follows:

$$\frac{100 \times 31.02}{M} = 15.0$$

$$M = 206$$

The molecular weight of Alkali Lignin A can also be calculated from that of the bromphenol compound by allowing for the presence of bromphenol and adding one mole of water (1321 − 173 + 18 = 1166). Since the molecular weight of Alkali Lignin A is approximately 1170 and that of the smallest unit containing one methoxyl group is 206, it is evident that six methoxyl groups must be present in the minimum Alkali Lignin A building unit, which therefore has a molecular weight of 6 × (206) = 1236, a value in good agreement with that calculated independently from the bromphenol lignin analyses.

In order to arrive at a formula for Alkali Lignin A containing six methoxyl groups, the smallest empirical formula must be multiplied by 6/0.48 (= 12.5), thus giving the empirical formula:

$$C_{67}H_{71}O_{23},$$

with a molecular weight of 1244, which agrees very well with 1166, the value found independently from the analytical data of the Bromphenol Alkali Lignin A. Since there are six methoxyl groups present in the original Alkali Lignin A, the bromphenol compound also contains the same number. Its calculated methoxyl value is therefore 13.3% and the bromine 5.71%, while the found values are 13.4% and 6.05% respectively.

The number of methoxyl groups, *x*, present in the diazomethane-methylated and those, *y*, of the fully methylated Alkali Lignin A can be calculated from the following equations:*

$$x = \frac{22.3 \times 12.5}{31.02} = 9; \; y = \frac{32.0 \times 12.5}{31.02} = 12.9$$

The ratio of hydroxyl to methoxyl to acetyl groups and the analytical data of the different derivatives found and calculated on the basis of the above formula for Alkali Lignin A are shown in Table I.

In contrast with the Willstätter- and Freudenberg-phenol lignins (3), Alkali Lignin A reacts with a smaller number of phenol molecules. From the experimental results obtained with Bromphenol Alkali Lignin A, it was found that a single bromphenol molecule reacts with the Alkali Lignin A to form an ether, and it seems permissible to assume that with the Phenol Alkali Lignin A a similar reaction occurs. The lower methoxyl content however indicates that a second phenol molecule must have reacted in a manner similar to that observed in the case of other phenol lignin derivatives(2). This is confirmed by the agreement between the analyses found for the Phenol Alkali Lignin A derivatives and the corresponding values calculated (Table II).

**22.3 and 32.0 are the per cent methoxyl found for diazomethane-methylated and for the fully methylated Alkali Lignin A respectively, while 12.5 is the multiplication factor used in connection with the minimum empirical formula (see page 104).*

TABLE III

SUMMARY OF EXPERIMENTAL AND THEORETICAL ANALYTICAL DATA FOR ALKALI LIGNIN B DERIVATIVES

Derivative	Ratio of hydroxyl to methoxyl to acetyl	Methoxyl content		Carbon content		Hydrogen content		Acetyl content	
		Found %	Calcd %	Found %	Calcd. %	Found %	Calcd. %	Found %	Calcd. %
Alkali Lignin B ($C_{108}H_{107}O_{37}$)	11 : 9 0	14 0	14 0	65 02	64 93	5 43	5 41	—	—
Acetylated Alkali Lignin B ($C_{130}H_{129}O_{48}$)	0 : 9 . 11	11 7	11 3	63 85	63 5	5 52	5 30	19 15	19 24
CH_2N_2-methylated Alkali Lignin B ($C_{116}H_{123}O_{37}$)	3 : 17 : 0	24 8	25 0	66 08	66 04	6 14	5 88	—	—
Acetylated CH_2N_2-methylated Alkali Lignin B									
($C_{122}H_{129}O_{40}$)	0 : 17 : 3	22 2	23 6	65 82	65 80	5 63	5 8	8 36	5 8
($C_{123}H_{129}O_{41}$)	0 : 16 : 4		21 9		65 25		5 74		7 6
Fully methylated Alkali Lignin B ($C_{119}H_{129}O_{37}$)	0 · 20 : 0	29 0	28 9	66 84	66 42	6 17	6 05	—	—

Experimental

ALKALI LIGNIN A

Preparation of Alkali Lignin A

Wood meal (180 gm.), previously extracted successively with benzene-alcohol, water and caustic soda solution (5%) was placed in a rotary iron digester with one litre of sodium hydroxide solution (4%), and the air replaced by nitrogen. The temperature was raised to 172° C. in 20 min., and maintained there for one hour. The solution was filtered off and the pulp washed with cold sodium hydroxide (1%). The combined filtrate was cooled, acidified with concentrated hydrochloric acid, and the precipitated lignin centrifuged off and dialyzed until neutral to Congo paper. The product was again centrifuged and dried to a thick paste on the suction filter. While still moist it was dissolved in dioxane, and the solution dried with anhydrous magnesium sulphate, filtered, and concentrated under diminished pressure to about 400 cc. The lignin was precipitated by adding this solution dropwise to about four litres of anhydrous ether. The precipitate was allowed to settle, the ether decanted off, and the lignin washed with dry ether, until the washings were colorless, and finally with petroleum ether (30–50° C.). It was centrifuged and dried. Yield, 35.6 gm., or 20% of the original wood meal.

The crude lignin from three such preparations had a methoxyl content of 14.2, 14.2 and 14.3% respectively. Analysis of purified material*;—Found: C, 64.5, 64.7, 64.7; H, 5.6, 5.8, 5.7; OCH_3, 14.9, 14.9, 14.9%. Calcd. for $C_{61}H_{45}O_{10}(OCH_3)_6(OH)_7$, [1244]: C, 64.6, H, 5.8; OCH_3, 15.0%.

Alkali Lignin A is a fine, light-brown powder, soluble in dioxane, pyridine, alcohol, acetone, glycol monomethyl ether, glacial acetic acid and sodium hydroxide, but insoluble in ether, petroleum ether, and benzene.

Acetylation of Alkali Lignin A

Alkali Lignin A (6 gm.) was dissolved in 30 cc. of pyridine, and 18 cc. of acetic anhydride added. After it had stood at room temperature for 50 hr. the solution was poured on to crushed ice. The precipitate was filtered off, washed with distilled water, and dried. Yield, 6.78 gm. The product was purified twice by dissolving it in dioxane, centrifuging, filtering and precipitating with ether. It was washed with ether and petroleum ether, and dried. Found: C, 64.2, 63.8; H, 5.4, 5.6; OCH_3, 12.2, 12.0; $COCH_3$, 21.7, 22.2%. Calcd. for $C_{61}H_{46}O_{10}(OCH_3)_6(OCOCH_3)_7$, [1538]: C, 63.2; H, 5.6; OCH_3, 12.1; $COCH_3$, 19.6%.

The acetylated Alkali Lignin A is a light-brownish substance, insoluble in ether, petroleum ether, carbon tetrachloride, alcohol, and water, and soluble in dioxane, pyridine, acetone, chloroform, and ethyl acetate.

Methylation with Diazomethane

Alkali Lignin A (8 gm.) was dissolved in 60 cc. of dioxane and methylated with the diazomethane prepared from 15 cc. of nitroso-methyl urethane. This methylation process was repeated until there was no further increase in methoxyl content. The product was twice purified by precipitation of

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* *After five precipitations with dioxane-ether.*

TABLE III

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Derivative	Ratio of hydroxyl to methoxyl to acetyl	Methoxyl content		Carbon content		Hydrogen content		Acetyl content	
		Found %	Calcd. %	Found %	Calcd. %	Found %	Calcd. %	Found %	Calcd. %
Alkali Lignin B ($C_{108}H_{107}O_{37}$)	11 : 9 : 0	14.0	14.0	65.02	64.93	5.43	5.41	—	—
Acetylated Alkali Lignin B ($C_{130}H_{129}O_{48}$)	0 : 9 : 11	11.7	11.3	63.85	63.5	5.52	5.30	19.15	19.24
CH_2N_2-methylated Alkali Lignin B ($C_{116}H_{123}O_{37}$)	3 : 17 : 0	24.8	25.0	66.08	66.04	6.14	5.88	—	—
Acetylated CH_2N_2-methylated Alkali Lignin B									
($C_{122}H_{129}O_{40}$)	0 : 17 : 3	22.2	23.6	65.82	65.80	5.63	5.8	8.36	5.8
($C_{123}H_{129}O_{41}$)	0 : 16 : 4		21.9		65.25		5.74		7.6
Fully methylated Alkali Lignin B ($C_{119}H_{129}O_{37}$)	0 : 20 : 0	29.0	28.9	66.84	66.42	6.17	6.05	—	—

Experimental

ALKALI LIGNIN A

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Wood meal (180 gm.), previously extracted successively with benzene-alcohol, water and caustic soda solution (5%) was placed in a rotary iron digester with one litre of sodium hydroxide solution (4%), and the air replaced by nitrogen. The temperature was raised to 172° C. in 20 min., and maintained there for one hour. The solution was filtered off and the pulp washed with cold sodium hydroxide (1%). The combined filtrate was cooled, acidified with concentrated hydrochloric acid, and the precipitated lignin centrifuged off and dialyzed until neutral to Congo paper. The product was again centrifuged and dried to a thick paste on the suction filter. While still moist it was dissolved in dioxane, and the solution dried with anhydrous magnesium sulphate, filtered, and concentrated under diminished pressure to about 400 cc. The lignin was precipitated by adding this solution dropwise to about four litres of anhydrous ether. The precipitate was allowed to settle, the ether decanted off, and the lignin washed with dry ether, until the washings were colorless, and finally with petroleum ether (30–50° C.). It was centrifuged and dried. Yield, 35.6 gm., or 20% of the original wood meal.

The crude lignin from three such preparations had a methoxyl content of 14.2, 14.2 and 14.3% respectively. Analysis of purified material*;—Found: C, 64.5, 64.7, 64.7; H, 5.6, 5.8, 5.7; OCH_3, 14.9, 14.9, 14.9%. Calcd. for $C_{61}H_{48}O_{10}(OCH_3)_6(OH)_7$, [1244]: C, 64.6, H, 5.8; OCH_3, 15.0%.

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The acetylated Alkali Lignin A is a light-brownish substance, insoluble in ether, petroleum ether, carbon tetrachloride, alcohol, and water, and soluble in dioxane, pyridine, acetone, chloroform, and ethyl acetate.

Methylation with Diazomethane

Alkali Lignin A (8 gm.) was dissolved in 60 cc. of dioxane and methylated with the diazomethane prepared from 15 cc. of nitroso-methyl urethane. This methylation process was repeated until there was no further increase in methoxyl content. The product was twice purified by precipitation of

* *After five precipitations with dioxane-ether.*

the dioxane solution into ether. Found: C, 66.4, 66.6; H, 6.6, 6.9; OCH_3, 22.2%. Calcd. for $C_{61}H_{46}O_{10}(OCH_3)_9(OH)_4$, [1286]: C, 65.3; H, 6.1; OCH_3, 21.7%.

The methylated product is a light-yellow powder insoluble in sodium hydroxide, ether and alcohol, slightly soluble in acetone, and readily soluble in dioxane, chloroform and pyridine.

Acetylation of Alkali Lignin A Premethylated with Diazomethane

A portion (6.1 gm.) of the premethylated Alkali Lignin A (OCH_3, 22.2%) was acetylated and purified in the same way as Alkali Lignin A. Found: C, 66.3, 66.2; H, 6 6, 6 5; OCH_3, 19.5, 19.4; $COCH_3$, 10.7, 11.5%. Calcd. for $C_{61}H_{46}O_{10}(OCH_3)_9(OCOCH_3)_4$, [1454]: C, 64 4; H, 5.9; OCH_3, 19.2; $COCH_3$, 11.8%.

Complete Methylation of Alkali Lignin A by Deacetylation and Methylation of Completely Acetylated Alkali Lignin A

Acetylated Alkali Lignin A (4.0 gm.) was deacetylated and methylated as described in an earlier paper (3). Yield, 3.25 gm.

After five methylations the methoxyl content was constant. The product was precipitated twice by pouring the dioxane solution into dry ether. It was washed with ether and petroleum ether, and dried to constant weight. Yield, 2.2 gm. Found: OCH_3, 31 4, 31.4%. Remethylation with diazomethane did not change the methoxyl content.

Complete Methylation by Deacetylation and Methylation of Acetylated. Diazomethane-premethylated Alkali Lignin A

Acetylated, premethylated Alkali Lignin A (3.0 gm.) was deacetylated and methylated in the same way and subsequently treated with diazomethane. The analyses of the product were constant after the second precipitation. Found: C, 66.7; H, 6.3; OCH_3, 31.6, 31.5%.

ALKALI LIGNIN B

Isolation and Purification of Alkali Lignin B

Alkali Lignin B was isolated from the dioxane-ether mother liquors of Alkali Lignin A by adding the concentrated solution dropwise to 15 times the volume of the ether-petroleum ether mixture (1 : 1). A light-yellow flocculent precipitate was obtained which was immediately washed with dry petroleum ether, and dried in a vacuum desiccator. The product was purified from dioxane and benzene. Found: C, 65.0, 65.0; H, 5.4, 5.5; OCH_3, 14.1, 14.0%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_9(OH)_{11}$, [1996]: C, 64.9; H, 5.4; OCH_3, 14.0%.

Acetylation of Alkali Lignin B.

Alkali Lignin B (1.0 gm.) was acetylated and isolated as in the case of acetylated Alkali Lignin A. The product was purified twice from dioxane and ether. Found: C, 63.8, 64.0; H, 5.5, 5.5; OCH_3, 11.7, 11.7; $COCH_3$, 19.9, 19.2%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_9(OCOCH_3)_{11}$, [2458]: C, 63.5; H, 5.3; OCH_3, 11.4; $COCH_3$, 19.2%.

Methylation of Alkali Lignin B with Diazomethane

Alkali Lignin B (7 gm.) was methylated with diazomethane. After five methylations there was no further increase in methoxyl value. The product was twice purified by means of dioxane and ether. Found: C, 66.3, 66.1; H, 6.1, 6.1; OCH_3, 24.8, 24.9%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_{17}(OH)_3$, [2108]: C, 66.1; H, 5.9; OCH_3, 25.0%.

Acetylation of Alkali Lignin B Premethylated with Diazomethane

Diazomethane-methylated Alkali Lignin B (3.75 gm.) was acetylated as above and purified from dioxane and ether. Yield, 3.90 gm. Found: C, 65.8, 65.9; H, 5.6, 5.6; OCH_3, 22.3, 22.3; $COCH_3$, 8.4, 8.7%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_{17}(OCOCH_3)_3$, [2234]: C, 65.8; H, 5.8; OCH_3, 23.6; $COCH_3$, 5.8%.

Complete Methylation of Alkali Lignin B

Acetylated, diazomethane-premethylated Alkali Lignin B (2.0 gm.) was deacetylated and methylated with dimethyl sulphate and sodium hydroxide, and purified in the same way as that described for Alkali Lignin A. Found: C, 66.88, 66.84; H, 6.35, 6.17; OCH_3, 28.7, 28.9%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_{20}$, [2150]: C, 66.4; H, 6.1 OCH_3, 28.9%.

PHENOL ALKALI LIGNIN A

Preparation

Alkali Lignin A (5 gm.) was treated with phenol and hydrogen chloride as described by Buckland, Brauns, and Hibbert (3) for Freudenberg and Willstätter lignin. The product was purified twice from dioxane and ether. Found: C, 68.8, 68.7; H, 5.5, 5.4; OCH_3, 12.9, 13.0, 12.9%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_6(OH)_8(OC_6H_5)(C_6H_5OH)$, [1414]: C, 67.0; H, 5.8; OCH_3, 13.1%.

Acetylation

Phenol Alkali Lignin A (6 gm.) was acetylated with pyridine and acetic anhydride and the product purified twice by precipitation from dioxane solution by ether. Yield, 6.7 gm. Found: C, 66.3, 66.4; H, 5.4, 5.5; OCH_3, 10.3, 10.3; $COCH_3$, 22.1, 21.9%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_6(OCOCH_3)_8(OC_6H_5)(C_6H_5OCOCH_3)$, [1792]; C, 65.0; H, 5.6; OCH_3, 10.4; $COCH_3$, 21.5%.

Methylation with Diazomethane

Phenol Alkali Lignin A (4.1 gm.) was methylated with diazomethane to a constant methoxyl content and purified from dioxane and ether. Yield, 4 gm. Found: C, 68.7, 68.8; H, 6.0, 6.2; OCH_3, 25.7, 25.6%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_{11}(OH)_3(OC_6H_5)(C_6H_5OCH_3)$: C, 68.1; H, 6.3; OCH_3, 24.8%.

Acetylation of Phenol Alkali Lignin A Premethylated with Diazomethane

A portion (1 gm.) of the above product was acetylated with pyridine and acetic anhydride. Yield, 1 gm. Found: C, 68.0, 68.2; H, 6.0, 6.1; OCH_3, 24.1, 23.9%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_{11}(OCOCH_3)_3(OC_6H_5)(C_6H_5OCH_3)$, [1624]: C, 67.2; H, 6.1; OCH_3, 22.9%.

Complete Methylation of Phenol Alkali Lignin A

Acetylated Phenol Alkali Lignin A (3.9 gm.) was deacetylated and methylated as described for the fully methylated Alkali Lignin A. Yield, 2.3 gm. Found: C, 68.8, 68.4; H, 6.2, 5.9; OCH_3, 30.5, 30.4%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_{14}(OC_6H_5)(C_6H_5OCH_3)$, [1540]: C, 68.6; H, 6.5; OCH_3, 30.2%.

Preparation of p-Bromphenol Alkali Lignin A

Alkali Lignin A (2 gm.) was treated with *p*-bromphenol and hydrogen chloride and purified in the same manner as that described for the phenol lignin. Yield, 2.1 gm. Found: OCH_3, 13.6, 13.7; Br, 6.0, 6.1, 6.1%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_6(OH)_8(OC_6H_4Br)$, [1399]: OCH_3, 13.3; Br, 5.7%. The analytical data did not change after retreatment of the product with *p*-bromphenol.

Preparation of o-Bromphenol Alkali Lignin A

Alkali Lignin A (4.0 gm.) was phenolated with *o*-bromphenol in the same manner as that described in the case of *p*-bromphenol. Yield, 4.1 gm. Found: OCH_3, 13.4, 13.4; Br, 6.0, 6.0%. Calcd. for $C_{61}H_{44}O_8(OCH_3)_6(OH)_8(OC_6H_4Br)$, [1399]: OCH_3, 13.3; Br. 5.7%.

Action of 2% Methyl Alcohol-Hydrogen Chloride Solution on Alkali Lignin A

Alkali Lignin A (4 gm.) was dissolved in 30 cc. of dioxane and the solution added dropwise to 100 cc. of anhydrous methyl alcohol containing 2% by weight of hydrogen chloride. The lignin precipitated out as a flocculent yellow precipitate which gradually redissolved to form a very dark colored solution. The alcoholic solution was sealed in a bomb tube and heated for 48 hr. in a tilting oven at 80–90° C. The reaction mixture was filtered, the filtrate concentrated under diminished pressure to about 100 cc. and the product precipitated by adding the solution dropwise to one litre of distilled water. The brown flocculent precipitate was filtered and washed with water. It was dried and purified by dissolving in dioxane and precipitating with ether. Found: C, 66.3, 66.6; H, 5.7, 5.7; OCH_3, 20.4%. Calcd. for $C_{61}H_{46}O_{10}(OCH_3)_8(OH)_5$, [1272] : C, 65.1; H, 6.0; OCH_3, 19.6%.

Methylation of Methanol Alkali Lignin A with Diazomethane

A portion (0.75 gm.) of the above product was methylated with diazomethane to a constant methoxyl value. The filtered solution was concentrated and the product precipitated by adding the solution dropwise to ether. Remethylation did not increase the methoxyl content. Found: C, 67.2, 67.3; H, 6.1, 6.0; OCH_3, 28.6, 28.5%. Calcd. for $C_{61}H_{46}O_{10}(OCH_3)_{12}(OH)$, [1328]: C, 66,0; H, 6.3; OCH_3, 28.0%.

Preparation of Phenol Alkali Lignin B

Alkali Lignin B (3 gm.) was treated with phenol under the same conditions as those used with Alkali Lignin A. Purification of the Phenol Alkali Lignin B using dioxane and ether gave two products: (*a*) an ether-insoluble Phenol

Alkali Lignin B (yield, 1.4 gm.), and (*b*) an ether-soluble derivative (yield, 2.3 gm.). The ether-insoluble product was redissolved in dioxane and precipitated with ether. Found: C, 68.1, 68.4; H, 5.6, 5.5; OCH_3, 12.1, 12.4%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_9(OH)_{10}(OC_6H_5)(C_6H_5OH)_2$, [2260]: C, 66.8; H, 5.4; OCH_3, 12.4%.

Thus prepared, the ether-insoluble Phenol Alkali Lignin B is a finely divided dark brown powder, easily soluble in sodium hydroxide, dioxane, glacial acetic acid, pyridine, alcohol and methyl alcohol, and insoluble in petroleum ether, benzene, chloroform and water.

The ether-soluble Phenol Alkali Lignin B was isolated in the same manner as ether-soluble Alkali Lignin B. The ether-dioxane mother liquor was filtered off and evaporated completely to dryness under diminished pressure. The residue was dissolved in about 20 cc. of dioxane and precipitated by adding the solution dropwise to 300 cc. of dry benzene. A brown flocculent precipitate was obtained which was washed with several portions of petroleum ether, and then dried in the usual manner. Found: C, 67.8, 68.4; H, 5.7, 5.6; OCH_3, 11.4, 11.2%. Calcd. for $C_{99}H_{69}O_{17}(OCH_3)_9(OH)_{10}(OC_6H_5)(C_6HO_5H)_4$, [2448]: C, 67.2; H, 5.6; OCH_3, 11.4%.

The pure, ether-soluble Alkali Lignin B is a chocolate-brown powder soluble in acetone, methyl alcohol and dioxane, and insoluble in petroleum ether, benzene, chloroform and water.

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PRELIMINARY STUDY OF THE FRACTIONATION OF ISOTOPIC ISOMERS BY DISTILLATION[1]

By D. F. Stedman[2]

Abstract

Slight separations of some isotopic isomers have been achieved by equilibrium rectification. In the case of chlorine the total separation amounted to 0 048 atomic weight units; 28 6% of the O^{18} has also been removed from normal oxygen by the fractionation of water, and in a short run with liquid oxygen the normal concentration of O^{18} has been raised from 0 2% to 0 25%. The last-mentioned separation can be carried considerably further with present equipment.

CH_3D was synthesized. Its boiling point appears to be 0 5° C. lower than that of methane.

The vapor pressures of a 56 8% solution of D_2O were measured, and it is suggested that the published values of the vapor pressure of D_2O at temperatures lower than 40° C. may be slightly too high.

Experiments have been under way for two years with the object of separating isotopic isomers by fractional distillation of suitable liquids, and tests have so far been made using carbon tetrachloride, dichloromethane, water and liquid oxygen. As some partial separations have been achieved, it seems desirable to publish the present preliminary report.

The fractionating columns used in this work, which were originally developed for use with hydrocarbons, will shortly be described in detail. They have been calibrated very carefully with mixtures of normal and cyclohexanes, and show, with various vapor velocities, from 12 to 25 theoretical plates per foot of height, although this factor probably varies not only with vapor velocity but quite appreciably with operating temperature and the type of liquid being fractionated. The extent of this variation, especially the last form, is not at present known.

It has been shown that with a very wide variety of isotopic isomers a small boiling point difference exists, giving in general appreciable separations of substances boiling at low temperatures, and diminishing separation coefficients as the boiling point or experimental temperature becomes higher, and as molecular weights or complexity become greater. It would appear that sufficiently minute examination would show some separation of all such isomers even after ordinary distillation, and that the use of rectifying columns of approximately 400 theoretical plates should produce considerable separation in quite a number of cases.

Distillation of Carbon Tetrachloride

This substance should be very suitable for fractionation of the chlorine isotopes since the pure light, and pure heavy, molecules are quite symmetrical, and should therefore have a boiling point lower than that of the remainder. The heavy form however is present only to the extent of 0.4%, and may consequently be neglected at this stage.

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[1] *Manuscript received August 2, 1935.*
Contribution from the National Research Laboratories, Ottawa, Canada.

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Several distillations of carbon tetrachloride have been performed, using a 6 ft. column distilling at a rate of 20 cc. of reflux per min. and removing product at a reflux ratio of from 1500 to 3000, and it is found as expected that light chlorine concentrates at the start of such a distillation. The lightest chlorine so far recovered in this manner is 0.042 atomic weight units lower than normal.

A plot to an arbitrary zero point of the type of result obtained, from a distillation of 2750 cc. of carbon tetrachloride, is given in Fig. 1, and it might be mentioned that 1 cc. of product represents about one theoretical plate of separation, and that this curve covers a run of more than six weeks duration at a reflux ratio of about 3000 : 1. The curve is plotted on the basis of atomic weight of chlorine determined by density, assuming equal molecular volumes, and is actually divided into two portions, that below 30 cc., when lighter impurities are present in the product, and from 30 cc. up, when no impurities remain.

The freezing point, density, refractive index and boiling point of samples were taken during the run, the freezing points being taken to within 0.2°, densities to within 10^{-5}, refractive indices to within 5×10^{-5}, and boiling points to within 0.01°, and it was found that from 30 cc. onwards only the density shows any variation, this continuing to rise throughout the distillation.

This particular distillation was stopped soon after this point, as further separation was not being attained. The actual samples examined for atomic weight were obtained from 500 cc. distilled in a similar manner, distilling somewhat more slowly, as this increases the effectiveness of these columns, and taking the "light" sample as the initial 20 cc. after 48 hr. at total reflux (this sample contained a few cubic centimetres of impurities, but they were not removed, as it was desired to give no opportunity for isotopic exchanges). The whole 500 cc. was then fractionated off at a reflux ratio of 2000 : 1, and the final 20 cc. taken as heavy material. These were passed with steam and hydrogen through a quartz-packed combustion tube at 800° C., neutralized with sodium carbonate, recrystallized in platinum, and compared with silver by volumetric methods. A weight burette was used for the main addition of silver nitrate, and the utmost care exercised throughout. Checks agreeing to within ±0.002 units of atomic weight were obtained. The two samples gave results of −0.042 and +0.006 units, and during this run it was observed that almost all the fractionation is obtained during the first part of the treatment; the removal of light heads evidently leaves the residue slightly heavy, but the other isomers do not fractionate appreciably amongst themselves. From the abruptness with which fractionation ceases, there is almost a suggestion that something is working against an ordinary, or exponential, separation; thus the boiling points of the heavy isomers may alternate with the alternation of symmetry, *i.e.*, the molecule containing two atoms of each form of chlorine may show enough symmetry to boil at a slightly lower temperature than the totally unsymmetrical forms.

From the separation achieved, and the effectiveness of the column, the boiling point differences involved were calculated to be about 0.05° C.

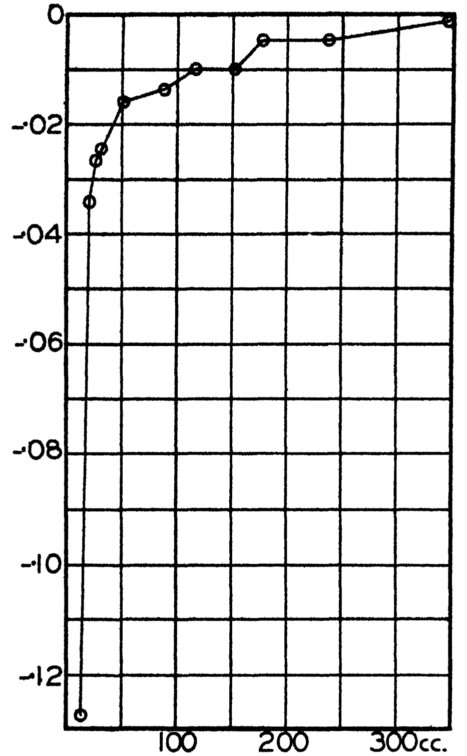

FIG. 1. *Atomic weights of chlorine in first fractions of carbon tetrachloride*

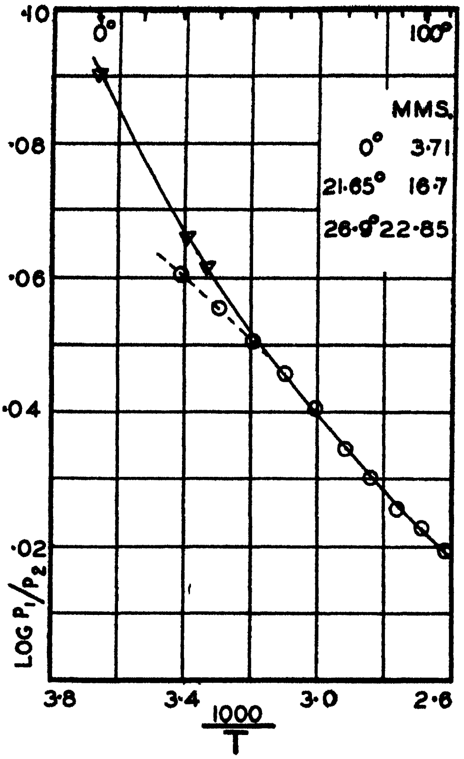

FIG 2. *Vapor pressures of D_2O H_2O Circles, values by Lewis and MacDonald*

Experiments on Dichloromethane

Dichloromethane (500 cc.) was distilled in a similar manner, but no very interesting results were obtained. The atomic weight remains normal within the accuracy of experiment throughout the distillation, until near the end, when it rises slightly. This curve resembles more the normal type, as heavy ends should be more readily separated than light heads. The final sample showed +0.023 units in atomic weight of chlorine. This distillation, since it corresponds to the normal exponential type, indicates an excessively small difference in boiling point, probably less than 0 01° C.

A previous attempt at separation, in which dichloromethane was distilled through a 40 plate column, has been reported by Henriques and Cornish (1). From consideration of their accuracy of density measurement, they estimate that the boiling point difference for each substitution of Cl^{37} for Cl^{35} cannot be more than 0.005° C. They state however that with liquids differing in boiling point by 5°, the time required for equilibrium to be established is 24 hr. Now, in an inadequate column, giving relatively small separations, this enrichment period is inversely proportional to the difference in boiling point, so that for 0.005° Δt, this period is 1000 days. They refluxed the dichloromethane for 117 hr., which is only 1/205 of the necessary time.

A consideration of the factors involved shows that their estimate of 0.005° C. must be raised by a factor of $(205)^{1/2}$ or 14.3, giving a figure of 0.07°, which they would just fail to detect in 117 hr., and as there are two substitutions possible the end members might differ by as much as 0.14° in boiling point, or 0.5% in vapor pressure, and still have escaped recognition.

Experiments on the Distillation of Water

Many experimenters have reported changes in the isotopic ratios of hydrogen and oxygen by the distillation of water, and it appeared that very interesting concentrations could be obtained fairly readily with the columns available here. It was therefore decided to test the boiling point differences by determining the rate of removal of the "heavy impurities", H_2O^{18}, H_2O^{17}, and D_2O or HDO, from the still head at total reflux.

The equation giving the time necessary to remove one-half of the impurity, assuming that α, the separation coefficient, approaches 1, and that the column is infinite, is

$$T_{1/2} = \frac{0.6932\, v\alpha}{V(\alpha - 1)^2},$$

where v is the volume of liquid retained in the column per theoretical plate, V is the volume distilled per unit time, and $\alpha = 1 + 0.036\, \Delta t$ for water.

A further experiment was also made with the object of determining the effective vapor pressure of HDO, comparing the vapor pressure of 6.68 and 56.8% solutions of D_2O with that of ordinary water. These vapor pressures were measured in a differential tensimeter, after the water had been degassed thoroughly by repeatedly freezing, evacuating and melting it. The vapor pressures were read on a differential mercury manometer with a cathetometer. The boiling point of the 6.68% solution was also compared with that of water at higher temperatures by means of a pair of boiling point stills, using double vapor-jacketed thermometers, and a differential thermocouple sensitive to 10^{-4} degrees.

At temperatures higher than 40° C., the mixture rule is evidently obeyed without regard to the formation of HDO, as the vapor pressure differences can be predicted by calculation from the results of Lewis and MacDonald (4), assuming the mixture rule. At lower temperatures a discrepancy appears, but if it is assumed that the mixture rule is still valid and the vapor pressure of pure D_2O is calculated from the present values, the results give a smooth curve without inflection if plotted as $\log p\ H_2O - \log p\ D_2O$ against $1/T$ in the usual manner, while the published values give a curve with inflection. It is therefore suggested that with the very small samples originally used for these measurements, a somewhat inadequate degassing procedure was used, resulting in a small increment of gas pressure with the D_2O. This would be important only at low temperatures.

Measurements were made from 0° C. (owing to supercooling the D_2O solution rarely froze), and these vapor pressures extrapolated from 56.8% to pure D_2O, as shown in Fig. 2. This extrapolation procedure may give erroneous results, as it may possibly be the mixture rule that fails at these temperatures, but the smooth curve obtained is very suggestive. This point evidently should be checked more closely, preferably on a fairly large sample of pure D_2O.

A recent attempt has been reported by Wahl and Urey (7) to determine the effective vapor pressure of HDO, using the distillation separation coefficient from H_2O, but one serious drawback of the method used is the fact that equilibrium is established very slowly across a liquid-vapor interface, or in other words, the liquid superheats. From superheated surfaces there is always a diffusion separation, added to equilibrium fractionation, and this method has in the past been used very successfully to achieve partial separation in several cases where equilibrium fractionation is certainly not responsible for the result. Now, in the case of H_2O : HDO, the diffusion coefficient to vacuum is 1.027, and for H_2O^{16} : H_2O^{18}, 1.054.

Their statement regarding pressure control would suggest that 1 mm. pressure variation had no particular effect, and this, combined with the statement that heating was adjusted "so that evaporation took place as fast as possible without ebullition," would suggest that the amount of superheating of the liquid was considerable, as these conditions are those that cause the maximum superheating.

In all probability the major portion of the separation coefficient observed for O^{18} is due to this cause, and the separation coefficient for deuterium is somewhat high for the same reason. The very great increase in the value of α for H_2O^{16} : H_2O^{18} at reduced temperatures also bears out the suggestion that superheating was very serious; thus from their figures, a reduction from 23° to 11° adds 50% to the separation coefficient, an exceedingly unlikely contribution, while it is in just this temperature range that superheating will become very serious.

As a result of the fact that at temperatures higher than 40° C. the mixture rule is obeyed for solutions of D_2O, it seems essential to assume that the normal boiling point of HDO is 100 71° C., and α should therefore be 1.0256 at 100° C. Although the fractionating columns have not been calibrated with water, in all probability they should contain about 0.8 cc. of water per theoretical plate; water was distilled at 18 cc. per min., and therefore from the above equation $T_{\frac{1}{2}}$ (H_2O : HDO) = 48 min., and this time should be inversely proportional to the square of boiling point differences for the various heavy constituents.

In order to determine the boiling point differences effective in water by direct experiment, 2000 cc. of water was refluxed in a 16 ft. column, starting with the column at 100° C. to avoid initial reflux. Samples were taken at various times during 12 days, and their densities determined, but instead of the type of result expected the density simply dropped slowly for about seven days, reaching about 79 p.p.m. difference. Owing, however, to the fact that these columns contain very little liquid, quite small samples must be taken (8 cc.); the purification of this presents quite a serious problem, and the densities measured were therefore not perfectly satisfactory in deciding the distillation characteristics of dilute solutions of D_2O or HDO. A sample of oxygen prepared from the lightest water was, however, sent to Dr. W. Bleakney of Princeton University, who kindly tested the $O^{16} : O^{18}$ ratio. He reported a change from the normal 500 : 1 to 680 : 1 (±10), or a removal of 26.5% of the original O^{18}, which is in all probability combined with the removal of 13.25% of the O^{17}, as this will naturally be twice as difficult to separate. On the basis of 1 : 2400 for O^{17}, water made from oxygen of this composition would give a density difference accounted for of 59 and 3 p.p.m. for O^{18} and O^{17}, respectively, or 62 p.p.m. altogether.

Another experiment was therefore carried out in which 7300 cc. of water was distilled with the 16 ft. column, at a reflux ratio of 100 : 1, this being twice that theoretically necessary with an infinite column for complete separation of HDO if its effective boiling point difference is 0.71° C. (4), and should therefore permit almost maximum separation with a finite column. The results are given in Table I and are comparable to ±2 p.p.m., and show the densities of samples after removing various volumes of product, the drop in density in the last two samples being evidently due to the method of collection—by circulating air through the condenser and finally the column and still pot.

TABLE I

DENSITIES OF FINAL FRACTIONS OF WATER

Cc.,	5455	6305	6855	7126	7274	7291	7308
P.p.m.	−9 5	−0 1	+26 4	+27 6	+71 6	+69 2	+63 8

The effects to be expected from this distillation were calculated before the experiment, and should have given in the final 20 cc. a density rise of over 2500 p.p.m. due to deuterium alone. Undoubtedly most of the 70 p.p.m. can be accounted for by a mass-spectrographic estimation of oxygen isotopes, as it has been demonstrated that the column separates these in a predictable, although slow, manner.

Another experiment was then carried out in which 2000 cc. of water was distilled at a reflux ratio of 1500 : 1, and the density of the last 500 cc. taken. It was however only 17.8 p.p.m. heavy. This again can be accounted for on the basis of oxygen isotope separation; even if it were entirely due to deuterium, a 50% loss is indicated. This loss would certainly not occur if the effective boiling point of HDO were 0.7° C. high.

It is evident that the distillation characteristics of dilute D_2O solutions are not predictable on the basis of present knowledge of the vapor pressures of the pure substances, although deviation from the ideal seems improbable.

It might also be mentioned that a test was also carried out under vacuum at 5 cm. of mercury at total reflux. Unfortunately a very slight leak persisted, and as a month was needed to establish equilibrium, the leak reduced the efficiency so much that the final sample, also examined by Dr. Bleakney, was almost identical with the similar sample obtained in eight days at atmospheric pressure. Calculations made on the basis of the known rate of leak, indicated that this experiment, if repeated, could be used to provide water containing only 30% of the normal O^{18}, but only about 2 cc. could be removed per week. This would undoubtedly have been attempted except for the fact that a better method of accomplishing the same end has been devised and is now being persued, although these experiments have made available quite appreciable quantities of water with a definite separation of the oxygen isotopes. In the near future it is intended to attempt to identify some of the O^{17} and O^{18} lines in the OH or other suitable oxygen spectrum, as they might offer a rapid, if somewhat approximate, analytical method.

It might be mentioned however that the rate of separation, and total separation obtained for $H_2O^{16} : H_2O^{18}$ both indicate a boiling point difference of only 0.04° C., or 0.14% in vapor pressure, in contrast with more than double this value suggested by Wahl and Urey (7).

Experiments with Methane

In order to test a possible cheap source of large amounts of deuterium, CH_3D of 56.8% purity was synthesized and the boiling point of this gas determined in a Podbielniak distillation apparatus. It was found to be 0.3° C. lower than that of the ordinary gas, or assuming ideal solution, as is certainly valid in this case, owing to the lack of polarity, the pure gas would boil at a temperature lower by 0.5°. This corresponds to 4% higher vapor pressure, which would indicate a fairly readily separable mixture. Thus, it is suggested that an almost unlimited quantity of methane under pressures as high as 1800 lb. per sq. in., such as that existing in certain oil fields, *e.g.*, the Turner Valley, Alberta, should provide a fairly cheap source of deuterium, if this pressure were utilized to liquefy and fractionate the gas by means of a heat exchanger and fractionating column similar to a liquid air fractionating machine. Such a column, to handle 1,000,000 cu. ft. of free methane per day, would have to be about 3 ft. in diameter and 10 ft. high, and would, with 50% yield, produce two litres of D_2O per day, virtually without labor or power costs. It is intended to test this separation as soon as a suitable column can be spared from the work on oxygen distillation.

Experiments with Oxygen

If water were to be distilled for the purpose of separating oxygen isotopes, the most economical procedure would be to increase the height of the present column to about 50 ft. and decrease the reflux rate to about 5 cc. per min. A long time would be required for the construction of such a column. A very long time would be necessary for equilibrium to be established, and although the column would provide a small supply of almost pure O^{16}, the rate of accumulation of O^{18} would be very low. It was therefore decided to reconstruct th us for the distillation of liquid oxygen directly, as by analogy rmous separation coefficient of $H_2 : D_2$, and the effect of tem- the vapor pressures of $H_2O : D_2O$, etc., it would appear that cules and low temperatures are favorable for such separations.

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Two recent notes by Klar and Kraus (3), and Smith (5), show such separation to be feasible. The results of Klar and Kraus show very large separation coefficients, but suffer from the drawback that the oxygen entering the liquefier must have been seriously abnormal, as the totals are far from balancing. Smith, however, suggests smaller variations, and although no data are given checking the balance of such separations, the figures given seem about of the order that might be expected.

Thus, the use of these figures and the estimation that the oxygen contained 0.5% of nitrogen, suggests that the vapor pressure of O^{18} is about 1.5% less than that of O^{16}, and that therefore O^{18} and O^{16} should be separated readily in these columns.

A 16 ft. column was therefore provided with a wrapping of aluminium foil, and a vacuum jacket, and liquid air was used in the condenser. Although all the experimental difficulties are not yet solved, some interesting results are being obtained. Thus in the latest run, of 27 hr. of operation the last six were under complete control of reflux, and a sample taken from the pot after this time, and examined by Dr. Bleakney, shows a 25% separation, the ratio $O^{16} : O^{18}$ being only 400 (± 2) instead of the usual 500.

The amount of liquid O_2 in the pot can be estimated only, but was probably in the neighborhood of 50 cc. (8 cu. ft. of gas is used for each run), so that about 0.025 cc. of liquid O^{18} is concentrated in six hours, or 0.1 cc. per day. In contrast with this is the change of 17.8 p.p.m. in density in the still pot during 60 days distillation of water; as the pot then contained 500 cc. of water this corresponds to the collection of only 0.08 cc. of H_2O^{18} in 60 days.

Only heavy samples of oxygen have been collected in a satisfactory condition, as unfortunately the still got out of control before light samples could be collected. If light samples had been obtained in a suitable condition there seems little doubt that a very substantial removal of O^{18} would have been shown, and it is therefore hoped that separation of these important isotopes may prove feasible without requiring the electrolysis of the ocean (2).

Acknowledgments

The author takes this opportunity of expressing his thanks for assistance received from many sources: to Dr. W. Bleakney, Princeton University, for his mass-spectrographic analyses; to Mr. J. O. Wilhelm, University of Toronto, for advice on the construction of apparatus for use at low temperatures; and to Mr. B. J. Kenalty for assistance during night runs with the liquid oxygen stills.

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THE ELECTROLYTIC PREPARATION OF ANTHRANILIC ACID[1]

BY J. W. SHIPLEY[2] AND J. M. CALHOUN[3]

Abstract

The electrolytic reduction of *o*-nitrobenzoic acid in alcoholic sulphuric acid at a lead cathode was investigated. The effect of various experimental conditions was studied and a maximum yield of 92% of amine obtained under favorable conditions. No evidence of the reduction of the carboxyl group was observed.

Introduction

The electrolytic reduction of *o*-nitrobenzoic acid has been studied only to a very limited extent. It has a theoretical interest because of the two unsaturated groups, the nitro and the carboxyl, since the presence of one, particularly in the ortho position, may influence the reduction of the other. The nitro group is reduced much more readily than the carboxyl and hence it should be possible, by regulation of the cathode potential, to reduce the nitro group while the carboxyl group is left intact, and so produce anthranilic acid. There is an additional interest in this reduction because of the commercial importance of anthranilic acid in the synthesis of indigo.

Löb (7) in 1896 reduced a solution of *o*-nitrobenzoic acid in sodium hydroxide solution, using platinum electrodes, and obtained a mixture of 50% of *o*-azoxybenzoic acid and 5–10% of *o*-hydrazobenzoic acid. A few years later Mettler (8) reported the reduction of both anthranilic acid and *o*-nitrobenzoic acid to *o*-aminobenzyl alcohol in 20–30% alcoholic sulphuric acid at a lead cathode at 20–30°C. with a current density of 6–12 amp. per sq. dm. Apparently both the nitro and carboxyl groups yielded to reduction.

The most recent work is due to Alvarez (1) who reported the preparation of anthranilic acid in 1928 by the electrolytic reduction of *o*-nitrobenzoic acid. Alvarez used as catholyte a solution of 60 gm. of *o*-nitrobenzoic acid in 20 cc. of alcohol and 100 cc. of sulphuric acid (20° Baumé). The anolyte was sulphuric acid (100 cc.) of the same concentration. Lead electrodes were used, the cathode being purified by electrolysis. A current of 8 amp. was passed for 7.5 hr. at a current density of 0.1 amp. per sq. dm. This corresponds to an excess of 4% of the quantity of electricity theoretically required.

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[1] *Manuscript received April 9, 1935.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada.

[2] *Professor of Chemistry, University of Alberta.*

[3] *Honors Student, University of Alberta.*

It is difficult to understand how so low a current density could be used successfully since a cathode 40 sq. dm. in area would be required, which is much too large for the volume of solution. The solubility of *o*-nitrobenzoic acid in a solution of the same volume and composition was found to be less than 15 gm. even at 90° C., so that most of the depolarizer must have been in suspension, a condition notably inefficient. Alvarez does not mention the temperature used, whether the catholyte was stirred, or the yields obtained.

Since both Mettler and Alvarez used virtually the same experimental conditions, other than current density and temperature, with such widely different results, it was thought that a more thorough investigation of the reduction would be of value.

Experimental

It was decided to conduct the reduction with lead electrodes in acid solution. This procedure tends to favor amine formation, since lead is a metal of high hydrogen overvoltage, thus making complete reduction of the nitro group possible. The use of an acid, rather than an alkaline, electrolyte necessitates the addition of alcohol to dissolve the *o*-nitrobenzoic acid, but the formation of any azoxy and azo derivatives in the reduction is reduced to a minimum.

The apparatus in which the reduction was carried out consisted of a 600 cc. Pyrex beaker in which was placed a porous cup 10 by 5 cm. to serve as the cathode chamber. The cathode was a cylinder made of 1 mm. sheet lead which just fitted inside the porous cup and was rotated by a small motor. Electrical connection was made through a mercury seal.

The anode was a second lead cylinder which fitted inside the annular space between the porous cup and the walls of the beaker. A thermometer was suspended in the anode compartment. The beaker was insulated with asbestos and heat was applied by means of a controlled Bunsen burner. A d-c. generator supplied current at 5 amp. and 120 volts.

Before each reduction the cathode was specially treated according to the method of Tafel (10). After washing in 20% sodium hydroxide solution it was electrolyzed as the anode in 20% sulphuric acid for 30 min. at a current density of 2 amp. per sq. dm. It was then washed with water, immersed in boiling water for several minutes, dipped in alcohol and air dried. The effect of this treatment was to free the cathode from traces of metallic impurities which would lower the hydrogen overvoltage and render it useless for a vigorous reduction. In addition the cathode surface was covered with a layer of oxide which in the first few minutes of the run was reduced to a thin membrane of spongy lead. According to Brockman (4), the spongy lead has a catalytic effect on the reduction.

The *o*-nitrobenzoic acid was obtained from two sources: One, a c.p. commercial product, melted at 146–146.5° C. (corr.) and the second, prepared in the laboratory by the oxidation of *o*-nitrotoluene with potassium permanganate by the method of Reimer and Gatewood (9), melted at 146.5–147° C. (corr.). The melting point of *o*-nitrobenzoic acid reported in the literature (6) is 147.5° C.

Analytical

The amount of amine produced in the reductions was determined by the titration of an aliquot portion of the reduction product with 0.05 *M* sodium nitrite solution, using potassium iodide-starch paper as indicator. The sodium nitrite solution was standardized against potassium permanganate and checked against pure anthranilic acid. It was found, in agreement with Bradt and Frost (2), that the permanganate method gave a value slightly too high.

The diazotization was carried out at 5–10° C. A 25 cc. aliquot was diluted to 50 cc. with water and 3 cc. of hydrochloric acid added. Standard sodium nitrite was then run in until a drop of the solution touched to the potassium iodide-starch paper indicated the end point. It was necessary to add the sodium nitrite slowly because of a slight lag in the establishment of the end point. Later it was found that the use of 0.1 *M* sodium nitrite and a larger aliquot gave a more satisfactory end point.

Effect of Temperature

The procedure followed was similar to that described by Bradt and Hart (3) for the electrolytic preparation of 3-amino-4-hydroxytoluene. The effect of different experimental conditions on the yield of amine was determined by making series of reductions, varying only one condition at a time.

The effect of temperature is shown in Table I and Fig. 1. It will be noted that the yield of amine increases with the temperature to a maximum of 88% at 80° C. At higher temperatures the yield drops off slightly owing to the proximity of the boiling point (92° C., 700 mm.) and the fact that *o*-nitrobenzoic acid is slightly volatile.

At temperatures between 40° and 80° C. the curve obtained (Fig. 1) is virtually a straight line, indicating that the yield of amine is directly proportional to the temperature. This is analogous to purely chemical reactions. At temperatures progressively lower than 40° C. the yield of amine rapidly drops off, owing to the fact that the *o*-nitrobenzoic acid was not completely soluble, a portion of it remaining in suspension.

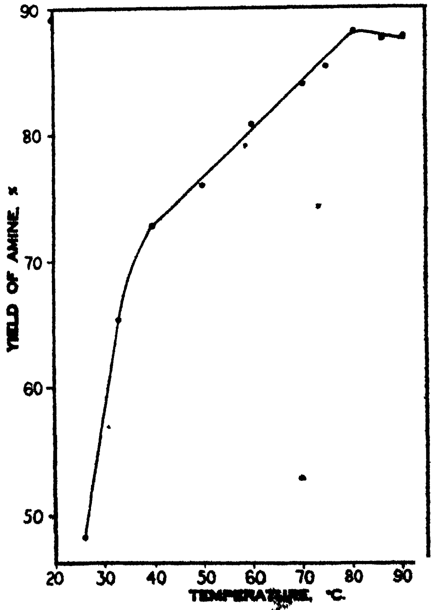

FIG. 1. *Effect of temperature on yield of anthranilic acid.*

TABLE I

EFFECT OF TEMPERATURE

Temp., °C.	E.m.f. across cell after 10 min., volts	Av. time during which H_2 was evolved, %	Yield of amine, %	Av. yield of amine, %
26	4.1	100	48.3	48.3
33	3.2	73	65.5	65.5
40	3.0 3.1	51	72.6 73.0	72.8
50	3.2 3.4	30	75.8 76.4	76.1
60	3.0 2.8	30	81.6 80.5	81.0
70	3.1 3.1	28	84.4 84.0	84.2
75	3.0 3.2 3 0	25	85.3 85.1 85.5	85.3
80	2.8 2.6 3.0 3.0 2.9	24	88.9 88.8 87.5 87.5 88.2	88.2
86	3.2 3.0	24	87.3 87.9	87.6
90	3.0 2.9	23	88.3 87.1	87.7

Cathode, lead cylinder 2.5 by 6 cm. Anode, same, 6 by 3 cm. Catholyte, 2.000 gm. o-nitrobenzoic acid, 40 cc. of 96% ethanol, 80 cc. of 25% sulphuric acid. Anolyte, 300 cc. of 25% sulphuric acid. Rate of stirring, about 150 r.p.m. Quantity of electricity, 1 926 amp.-hour (theoretical quantity of electricity calculated for the complete reduction of NO_2 to NH_2 in 2 gm. of o-nitrobenzoic acid). Cathodic current density, 2.0 amp. per sq. dm. (both sides).

The evolution of hydrogen represents a loss in current efficiency (current efficiency and yield of amine are equivalent when the theoretical quantity of electricity, in this case, 1·926 amp.-hr., is passed through the solution). Column 3, Table I, shows that the time during which hydrogen is evolved decreases as the temperature and efficiency rise. At 26° C. hydrogen is evolved during the entire reduction period, while at 80° C. evolution occurred only during the last quarter of the period. At the lower temperatures the velocity of reduction is not sufficiently great to absorb all the hydrogen as rapidly as it is produced. This results in greater evolution of hydrogen and lowered current efficiency. It is therefore probable that in the experiments at lower temperatures, the material unaccounted for in the analysis is unreduced *o*-nitrobenzoic acid and not products of secondary reactions.

Effect of Current Density

Table II and Fig. 2 show the effect of cathodic current density on yield of amine. At current densities greater than 5 amp. per sq. dm. it was necessary to use a smaller cathode, since the maximum current available was 5 amp.

TABLE II

EFFECT OF CURRENT DENSITY

Cathodic current density, amp./dm.^{2}	E.m.f. across cell after 10 min., volts	Av. time during which H_2 was evolved, %	Yield of amine, %	Av. yield of amine, %
0.5	2.3	9	88.3	88.3
1.0	2.6 3.6 3.4 2.5 2.6	13	89.8 90.3 87.6 88.5 88.8	88.9
1.5	2.6 2.6 2.7	18	88.9 87.7 88.9	88.5
*2.0		24		88.2
2.25	2.6 2.8 2.8	26	89.6 88.2 86.6	88.1
2.5	2.9 3.0 3.0	26	88.3 86.4 90.0	88.2
3.0	3.7 3.0	25	87.2 87.3	87.3
4.0	4.0 3.9	35	86.0 86.2	86.1
5.0	3.9 3.0	61	85.4 85.4	85.4
**6.0	3.4 3.9	28	84.0 84.3	84.2
**8.0	4.1 3.6	42	81.1 79.8	80.5
**10.0	4.8	57	77.6	77.6

Temp., 80°C. Other conditions as given in Table I.
**See Table I for details. **Cathode 2.5 by 3 cm.*

A maximum yield of 89% was obtained at a current density of 1 amp. per sq. dm. At a lower current density a smaller yield resulted, probably owing to the longer time required for the reduction, which would permit loss of *o*-nitrobenzoic acid by diffusion to the anode chamber. Increase in current density resulted in an increase in the amount of hydrogen evolved and a corresponding decrease in efficiency.

It should be pointed out that current density measurements are only approximate at best. This is because the effective area depends on the condition of the surface of the metal, which is impossible to measure or duplicate exactly. However, for a given current the apparent surface area is a useful measure of the current density.

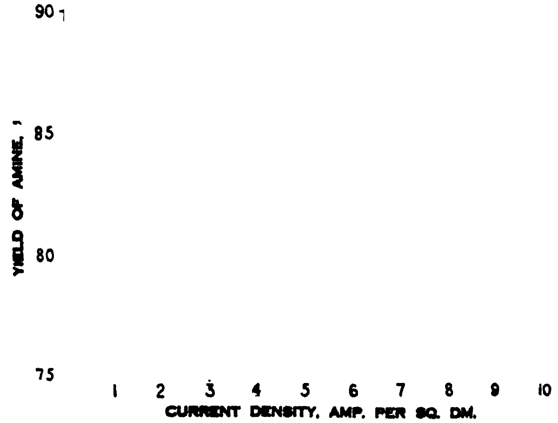

FIG. 2. *Effect of current density on yield of anthranilic acid.*

Effect of Electrolyte Composition

The data showing the effect of electrolyte composition on yield of amine are given in Table III. In each case the anolyte consisted of sulphuric acid of the same concentration as that used in the catholyte. It was found that one part of 96% alcohol in the catholyte to two parts of sulphuric acid solution gave the best results. A decrease in the amount of alcohol lowered the solubility of *o*-nitrobenzoic acid, and an increase lowered the boiling point of the solution, necessitating the use of a lower temperature.

TABLE III

EFFECT OF ELECTROLYTE COMPOSITION

Catholyte composition	E.m.f. across cell after 10 min., volts	Av. time during which H_2 was evolved, %	Yield of amine, %	Av. yield of amine, %
25 cc. alcohol; 100 cc. 25% H_2SO_4	2.9	17	86.8	86.8
*80 cc. alcohol; 40 cc. 25% H_2SO_4	3.0	31	83.8	83.8
40 cc. alcohol; 80 cc. 2% H_2SO_4	3.3	23	85.4	85.4
40 cc. alcohol; 80 cc. 5% H_2SO_4	2.9	15	90.2	90.0
	3.0		89.8	
40 cc. alcohol; 80 cc. 10% H_2SO_4	2.7	16	89.8	89.6
	2.7		89.3	
40 cc. alcohol; 80 cc. 15% H_2SO_4	3.0	16	88.8	88.8
40 cc. alcohol; 80 cc. 25% H_2SO_4		24		88.2
40 cc. alcohol; 80 cc. 35% H_2SO_4	2.9	33	85.1	85.1

Temp., 80°C. (except where otherwise stated). Other conditions as given in Table I.
**Temp., 75° C.*

The optimum concentration of the sulphuric acid solution was between 5 and 10%, and resulted in a yield of 90% of amine. A lower concentration of acid resulted in a marked decrease in yield, owing to the increased resistance of the electrolyte. At higher concentrations of acid the lowered efficiency was considered to be due to an increase in side reactions, such as condensations or rearrangements favored by the high acidity. This was borne out by the fact that the reduction product was colored a bright red, indicating the presence of azoxy or azo compounds.

Effect of Concentration of o-Nitrobenzoic Acid

Table IV shows the effect of the concentration of *o*-nitrobenzoic acid on the yield of amine. The optimum concentration was found to be 2 gm. in 120 cc. of solution (about 0.1 *M*). At lower concentrations, diffusion of *o*-nitrobenzoic acid to the cathode surface was not rapid enough, and hydrogen was evolved for 30% of the total time, resulting in a lowered efficiency. The efficiency probably could be increased by stirring the solution more rapidly.

TABLE IV

EFFECT OF CONCENTRATION OF *o*-NITROBENZOIC ACID

Weight of *o*-nitrobenzoic acid, gm.	E.m.f. across cell after 10 min., volts	Av. time during which H_2 was evolved, %	Yield of amine, %	Av. yield of amine, %
1.000	3.0 3.0	31	85.2 84.8	85.0
2.000	2 7 2 7	16	89.8 89 3	89.6
4.000	3.3 3.1	13	87.0 89.1	88.1
6 000	2.8	10	87.3	87.3

Temp., 80°C. Catholyte: 40 cc. of 96% alcohol, 80 cc. of 10% sulphuric acid. Anolyte: 300 cc. of 10% sulphuric acid. Other conditions as given in Table I.

Increasing the concentration of *o*-nitrobenzoic acid decreased the amount of hydrogen evolved, but there was not a corresponding increase in material yield when concentrations greater than 2 gm. were used. This may be due to the longer time required for reduction, which permits loss of *o*-nitrobenzoic acid by diffusion or volatilization.

Effect of Quantity of Current Passed Through the Solution

Since yield of amine is more important than current efficiency it was desirable to determine whether an excess of the theoretical quantity of electricity (1.926 amp.-hr.) would increase the yield of amine. The results are given in Table V.

TABLE V

EFFECT OF QUANTITY OF CURRENT PASSED THROUGH THE SOLUTION

Per cent theoretical current (1 926 amp.-hr.)	E.m.f. across cell after 10 min., volts	Time during which H_2 was evolved, %	Yield of amine, %	Av. yield of amine, %	Av. current efficiency, %
85	2.7 2.7	5	78.1 78.7	78.4	92.2
100	2.7 2.7	16	89.8 89.3	89.6	89.6
125	2.8 2.8	34	90.3 92.3	91.3	73.0

Temp., 80°C. Catholyte: 2 000 gm. of o-nitrobenzoic acid, 40 cc. of 96% alcohol, 80 cc. of 10% sulphuric acid. Anolyte: 300 cc. of 10% sulphuric acid. Other conditions as given in Table I.

When 85% of the theoretical quantity of electricity had been passed through the solution, very little hydrogen evolution had taken place. This resulted in high current efficiency but low material yields. After 100% of the theoretical quantity of electricity had been passed through, the material yield had considerably increased, indicating that reduction continued after hydrogen evolution began. When an excess of 25% had been passed through, the yield of amine had increased only slightly, and at the expense of a large decrease in current efficiency.

Effect of Cathode Surface

The velocity of reduction, and hence the yield of amine, depends to a large extent on the nature of the cathode surface. In an attempt to increase the yield, a coating of sponge lead was deposited on the cathode according to the directions of Bradt and Hart (3).

Lead monoxide (20 gm.) and sodium hydroxide (100 gm.) were dissolved in water to give a 300 cc. solution and the lead cylinder electrolyzed as cathode for about five minutes at a current density of 5 amp. per sq. dm. It was then washed with water, dilute sulphuric acid, and again with water. This procedure gave a very rough spongy surface.

TABLE VI

EFFECT OF CATHODE SURFACE

Cathode surface	E.m.f. across cell after 10 min., volts	Av. per cent time during which H_2 evolved	Yield of amine, %	Av. yield of amine, %
Smooth	2.7	16	89.8 89.3	89.6
Spongy	2.6	9	91.4 92.5	92.0

Temp., 80°C. Catholyte: 2.000 gm. of o-nitrobenzoic acid, 40 cc. of 96% alcohol, 80 cc. of 10% sulphuric acid. Anolyte: 300 cc. 10% sulphuric acid. Other conditions as given in Table I.

The results are shown in Table VI. The smooth cathode was prepared by anodic electrolysis as previously described. It is evident that an increase in yield of more than 2% is obtained with a spongy lead cathode, and at the same time the amount of hydrogen evolved is less. The effect of a spongy surface is in reality to lower the effective current density by increasing the surface area available to the depolarizer. The use of a spongy surface is more effective than decreasing the current strength, since the spongy surface does not require a longer time for the reduction, as would be the case with a plain cathode and a low current strength.

Separation of Reduction Products

Anthranilic acid was separated when desired from the combined products of a number of reductions. The solution was neutralized with an excess of sodium carbonate and the alcohol distilled off. It was then made slightly acid with acetic acid, filtered, and the filtrate extracted with ether.

The residue from the ether extraction was recrystallized from hot water, using animal charcoal for decolorizing. A white crystalline product which melted at 146° C. (corr.) was obtained, the acetyl derivative of which melted at 184.5° C. (corr.). The melting points reported in the literature (6) are: anthranilic acid, 145° C. and *o*-acetylaminobenzoic acid, 185° C.

An attempt was made to identify any *o*-aminobenzyl alcohol by the method of Mettler (8). The alkaline residue from the distillation of the alcohol was saturated with ammonium sulphate and extracted with ether. The ether layer yielded nothing but a trace of resinous material, indicating the absence of *o*-aminobenzyl alcohol. Ether extractions in acid solution yielded nothing but small amounts of unchanged *o*-nitrobenzoic acid.

The results of analysis show that anthranilic acid represented the major portion of the reduction product. However, the color of the solutions, which varied from pale yellow to cherry red, indicated the presence of other compounds, probably azoxy or azo derivatives, but in quantities too small to separate and indentify.

Discussion

The electrolytic reduction of *o*-nitrobenzoic acid in dilute alcoholic sulphuric acid at a lead cathode, under favorable conditions, has been shown to yield anthranilic acid in yields of more than 90%. The reaction may be represented by the equation:

$$NO_2.C_6H_4.COOH + 6H^+ + 6e = NH_2.C_6H_4.COOH + 2H_2O$$

It is assumed that the mechanism is analogous to that suggested by Haber (5) for the electrolytic reduction of nitrobenzene.

It is evident that under the foregoing experimental conditions the intensity of reduction was not sufficiently great to reduce appreciably the carboxyl group. It is possible that at a higher current density and lower temperature the formation of *o*-aminobenzyl alcohol as reported by Mettler (8) would be favored. However, the vigorous evolution of hydrogen at the completion of the reduction of the nitro group in the authors' experiments indicates that little, if any, additional reduction is taking place.

The maximum yield of amine obtained was 92%. The remaining 8% of material may be accounted for in loss by volatilization and diffusion to the anode chamber, by the fact that a small amount of *o*-nitrobenzoic acid remained unchanged and by the formation of products of various side reactions, such as azoxy and azo derivatives. It is not impossible that even higher yields of amine might be obtained. The addition of *o*-nitrobenzoic acid in successive portions as the reduction progresses and a decrease in the current density towards the end of the reduction, with perhaps the use of a small excess of current, would be expected to cause an increase in the amount of *o*-nitrobenzoic acid reduced. The use of addition agents or hydrogen carriers might also increase the yield. More rapid stirring might be advantageous, although, when the depolarizer is in solution, the effect of stirring at a rate greater than a certain minimum is small. Bradt and Hart (3) found that, in the electrolytic reduction of 3-nitro-4-hydroxytoluene, an increase of only 0·8% in the yield of amine was obtained when the rate of stirring was varied between 0 and 2000 r.p.m. after complete solution of the nitrocresol.

The limitations of the experimental results are considered to be chiefly analytical. The standardization of sodium nitrite by potassium permanganate gives values slightly too high, while the lag in the endpoint gives values slightly too low. Manipulative errors are due chiefly to the lack of an automatic temperature control and loss of solvent by vaporization. The use of a closed cell, fitted with a return condenser, and an automatic electrical heating device would be more satisfactory. The fact that more than 100 reductions were satisfactorily carried out shows that the process is highly successful if sufficient care is taken in the preparation of the cathode.

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THE SORPTION OF DIMETHYL ETHER ON ALUMINA[1]

By J. Edwards[2] and O. Maass[3]

Abstract

The sorption of dimethyl ether on alumina has been investigated at pressures from 0 5 to 52 atm., the critical pressure, over the temperature range 25–135° C. The results are comparable to those for the propylene–alumina system. No discontinuity in the sorption accompanies the transition of sorbate from vapor to gas at the critical temperature; this differs from the previous results for the liquid-to-gas change. The initial stages of the sorption involve the formation of a monomolecular layer followed, with increasing pressure, by a multimolecular layer of increasing depth. It is unlikely that condensation to liquid occurs in the pores except at high relative pressures. The increase in critical temperature of such a liquid must be exceedingly great to account for the continuous form of the isobars up to 135° C.

Introduction

Although there has been a great deal of experimental work done on the adsorption of vapors and gases by solids, relatively little has been carried out at pressures greater than atmospheric. Since the leading hypotheses regarding the nature of this phenomenon differ mainly in their predictions of the extent of adsorption in this region, data for a number of systems are highly desirable.

A recent contribution by Morris and Maass (9) on the adsorption of propylene by alumina contained data for a wide range of pressures including the critical one, and for a temperature range of 20–100° C. The interesting behavior of the system accompanying the transition of sorbate from liquid to gas led to further work in the critical region, and the results for the system dimethyl ether–alumina were recently published (5). These results dealt with the sorption of the liquid phase (below the critical temperature), and of the "persistent liquid phase" (above the critical temperature).

In the present paper the results obtained for the sorption of dimethyl ether on alumina from 0.5 to 52 atm., the critical pressure, are given for the temperature range 25–135° C. The sorption was measured throughout with the sorbate definitely in the vapor or gaseous state. While the previous paper (5) was of interest primarily for the information given regarding the critical phenomena, the present paper deals with the nature of the sorption process over a pressure range including high pressures.

Experimental

Alumina, prepared according to the method of Munro and Johnson (10), was selected as sorbent on account of its high porosity and rigid structure. In view of the well known physical properties of dimethyl ether at high pressures, and of its suitable critical constants which permit the use of glass

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada.

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apparatus, this substance was chosen as sorbate. The sample used throughout the present investigation was prepared and purified as described by Tapp, Steacie and Maass (16).

The apparatus employed was similar to that used by Morris and Maass (9), differing only in dimensions and thermostatic control, modified on account of the higher temperatures employed.

The McBain-Bakr balance had a sensitivity of 0.00376 gm. per mm. extension, a normal length of 57.66 mm.; the maximum load was 0.45 gm. The cathetometer used permitted weight measurements to within ±0.0004 gm.

The calculation of the sorption has been fully described elsewhere (5, 9). No correction was made for the buoyant effect of the quartz spiral itself, since under the conditions of the experiments this factor seldom exceeded 0.0001 gm., the greatest error being 0.00017 gm.

Results

Sorption is given in the usual form, x/m, where x is the number of grams sorbed per m grams of sorbent.

Although the sorption at low relative pressures appeared to reach an equilibrium value within the time necessary for the gel to attain thermal equilibrium with the container, longer times were often necessary at high relative pressures before no further extension of the spiral could be detected. In such cases there appeared to be no systematic behavior that could be used as a measure of the rate of sorption in its final stages. The nature of the apparatus does not permit mesaurements of sorption rates to be made throughout the whole course of the process.

The density of the vapor surrounding the sorbent was obtained from the data of Cardoso and Coppola (3). The determination of the densities at relative humidities less than 100% was made by assuming a linear relation between density and temperature at constant pressure. The error involved in this assumption was negligible at low pressures, and at high pressures was not serious, since in these cases the temperature range over which the calculations were made was small. In the region approaching the critical, the more recently obtained density values of Tapp, Steacie and Maass (16) were used. Pressure values were taken from the vapor pressure curve for dimethyl ether obtained by Cardoso and Bruno (2).

The values in Table I, selected from approximately 250 readings, indicate the manner in which the sorption varied with the temperature and pressure. The corresponding isobars and isotherms are illustrated graphically in Figs. 1, 2 and 3. In Fig. 3, in which the sorption has been plotted against the relative pressure, P/P_s, there is some uncertainty in the form of the curves near the saturation value. In the cases where the extrapolation was short it was considered justifiable to indicate the probable endpoint, though a

TABLE I

SORPTION OF DIMETHYL ETHER (x/m) ON ALUMINA AT VARIOUS TEMPERATURES AND PRESSURES

Gel temp., °C.	Pressure, atm.					
	0.45	3.9	19.0	27.5	38.5	45.6
30	0.0192	0.0338				
40	0.0176	0.0287				
50	0.0142	0.0244				
60	0.0123	0.0209				
70	0.0106	0.0182				
80	0.0084	0 0156				
90	0.0053	0.0127	0.0242			
100	0 0036	0.0098	0.0192	0.0292		
110	0 0023	0.0078	0 0159	0.0228		
115	0 0020	0 0072	0 0140	0 0203	0.0320	
120	0 0017	0 0066	0.0120	0 0184	0.0266	
124	0.0015	0.0063	0.0110	0.0167	0.0243	0.0310
126	0 0015	0 0062	0 0106	0.0158	0.0235	0.0290
128	0.0015	0 0061	0 0102	0.0132	0.0229	0.0277
130	0 0014	0 0060	0 0096	0.0145	0.0220	0.0268
135	0 0013	0 0058	0.0080	0.0136	0.0207	0.0252

sharper increase in $d(x/m)/d(P/P_s)$ has been found in some cases for other systems (1). However, the general form of the isotherms closely resembles that of the cellulose-water-vapor system curves (6) and of the active-silica –water,–benzene and –alcohol isotherms (13), in which cases the saturation value was approached in a manner similar to that indicated in Fig. 3. The point is of interest in that an estimation of the saturation value of the adsorption may yield important information regarding the pore volume of the sorbent. These data were utilized previously (5) in an attempt to consider the possibility that liquid might exist in the pores of the sorbent above the critical temperature of the sorbate in the bulk phase.

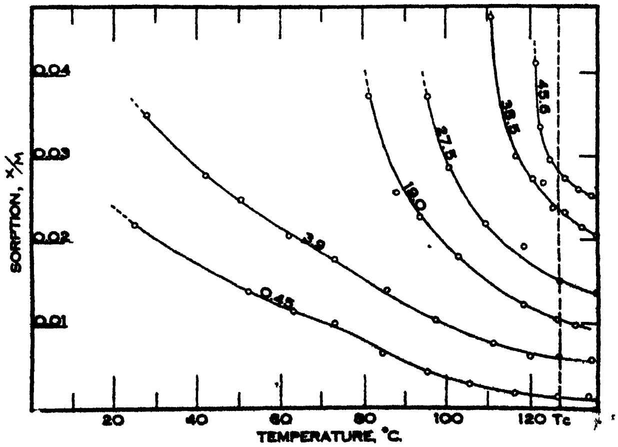

FIG. 1. *Isobars showing the sorption of dimethyl ether vapor and gas on alumina. Pressures in atmospheres.*

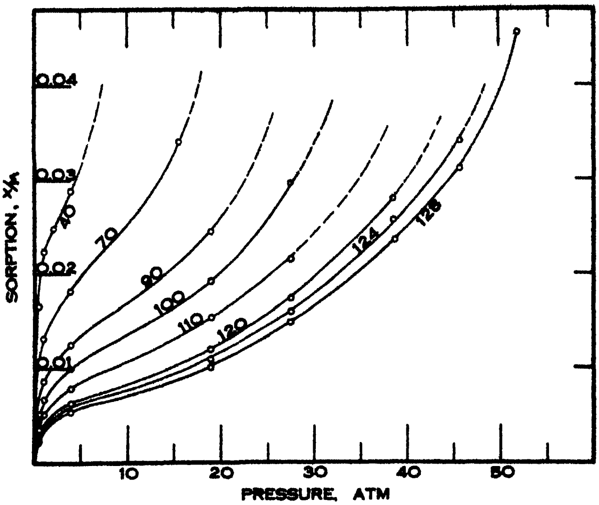

FIG. 2. *Isotherms showing the sorption of dimethyl ether on alumina. Temperatures in °C.*

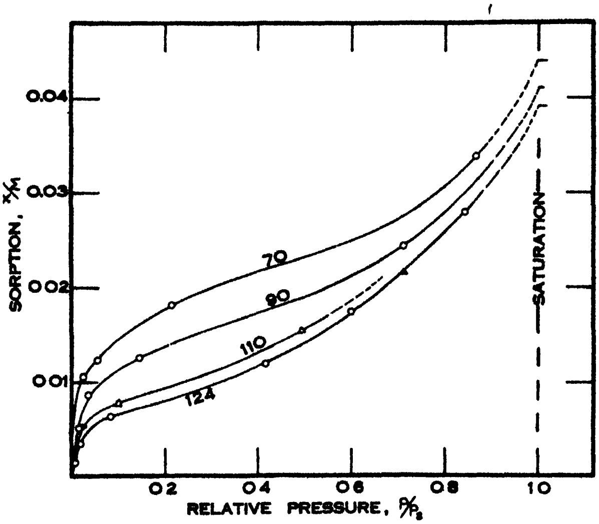

FIG. 3. *Isotherms showing the sorption of dimethyl ether on alumina. Temperatures in °C.*

Discussion

The form of the isobars and isotherms is similar in most respects to the forms of those of the propylene–alumina system. There is, however, a difference in the low-pressure region of the high-temperature isotherms: for the system propylene–alumina it is apparent that the first stage of the adsorption corresponds to the existence of a monomolecular layer forming a surface complex which is stable at high pressures throughout the temperature range studied, but which for low pressures breaks down at the higher temperatures. In the present system the slight inflections in the 0.45 and 3.9 isobars in the neighborhood of 80–100° C. indicate a tendency toward destruction of the surface layer, but the extent of this decomposition appears insufficient to be particularly noticeable in the high-temperature isotherms. The isobars indicate however that, for lower pressures, the surface complex would probably be unstable within the temperature range studied. Although this difference in behavior might be attributed to a higher heat of adsorption of dimethyl ether than that of propylene, the slope of the isosteres plotted semilogarithmically does not indicate this to be so, and it is very probable that the difference can be attributed to a difference in the alumina gels used in the two investigations.

In general the S-shaped isotherms may be interpreted according to the method of Rideal (15), whereby the first part of the curve corresponds to a monomolecular layer followed by a multimolecular one which has been regarded by Polanyi (14) as a thick, compressed film, and by others (11) as condensation to liquid in the capillary tubes of the sorbent. It can be readily demonstrated that the first stages of the sorption process are characterized by the formation of a monomolecular layer, by testing the results according to the Williams-Henry formula (7, 17). The equation for the isostere is $(\log x/mP) = k_1/T + k_2$, and in Fig. 4 the results have been

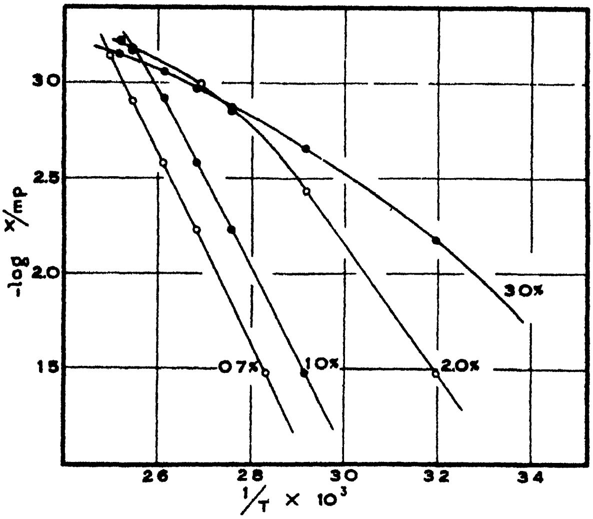

FIG. 4. *Isosteres for the dimethyl-ether–alumina system, plotted according to the Williams-Henry formula.*

represented for 0.7 to 3% sorption. The straight lines obtained in the 0.7% and 1% isosteres indicate that the sorption is exactly monomolecular, but for higher values of the sorption this is no longer true.

Following the region in which a monomolecular layer is formed, is the characteristic region of smaller slope, followed by the final region of increasing slope corresponding to a sorption tending toward saturation. From the point of view of the theory of capillary condensation, the isotherms of Fig. 3 indicate that the sorption tends to become independent of temperature at the higher relative pressures, a condition predicted by the hypothesis. (When the volume, rather than the weight of sorbate, is taken into consideration, still better agreement is obtained, except in the case of those isotherms very near the critical temperature.) Thus at high relative pressures it appears probable that condensation of the sorbate to a liquid of density approximately that of the normal liquid does occur.

It will be noticed (Fig. 3) that the inflection in the curve, following which the sorption tends to saturation, occurs at relative pressures as low as 0.2. McBain has shown conclusively that the theory of capillary condensation must break down under these conditions, for the Kelvin equation for the lowering of the vapor pressure requires that the radius of the capillaries be of the order of molecular dimensions (8, pp. 436-442). It is singularly forced to regard molecules as in the liquid state when they are in immediate contact with the wall.

Further evidence not in complete agreement with Patrick's hypothesis may be obtained from Fig. 2. The isotherms above and below the critical temperature are identical in form, and indeed an isotherm at 136° C. shows no break in sorption. Similar results with the carbon-dioxide-charcoal system led Patrick *et al.* (12) to the belief that the surface tension of the liquid in the capillaries was considerably greater than that of the normal liquid, resulting in an increased critical temperature of the capillary liquid. While the partial pressures studied by Patrick were so small that capillary condensation would not be expected to occur, the study of the present system has been made over all possible pressures, and it is interesting to consider the results in the light of this hypothesis. On the basis of an increase in the critical temperature of liquid in the pores, the magnitude of this effect would depend on the pore size, so that the form of the sorption isobar at temperatures higher than the normal critical temperature would be dependent upon the frequency distribution of pore sizes in the gel. When the critical temperature of the liquid in the smallest capillaries had eventually been reached, the density of the sorbed material would become equal to that of the material in the normal bulk phase. Since this is a gravimetric method and corresponds exactly to the definition of sorption, in that the excess of material in the vicinity of the sorbent over that present in an equal volume of bulk phase is considered as the amount sorbed, then under the final temperature conditions mentioned above, sorption would become zero. The fact that, at temperatures higher than the normal critical temperature, the sorption isobars (Fig. 1) show no decrease in sorption in excess of that given by the normal temperature coefficient, indicates that the Patrick conception cannot hold. There appears then to be no adequate interpretation of the similarity in form of the isotherms at temperatures higher than, and lower than, the critical temperature, and it becomes evident that the theory of capillary condensation cannot account for the experimental results. Since the relative pressure isotherms, taken at temperatures lower than the critical temperature, gave evidence at high values of the relative pressure that closely fits the requirements demanded by the theory, the possibility that the familiar S-shaped isotherms do not represent capillary condensation becomes apparent.

Substantiation of these results has been obtained by Morris and Maass (9), who demonstrated that even at a temperature of 15° C. higher than the critical temperature no change in the form of the isotherms took place. Coolidge (4) has recently extended the study of the carbon-dioxide–charcoal system to a high pressure range, and concluded that no break in the isotherm was apparent when the density of the sorbed phase itself was taken into account. A quantitative agreement with the Polanyi theory was obtained.

An interpretation of these results will await more complete data, and it is hoped that the study of other systems will be shortly carried out, and the behavior of these systems in the neighborhood of the critical temperature be compared with these and earlier results.

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THE VARIATION OF THE VISCOSITY OF GASES WITH TEMPERATURE OVER A LARGE TEMPERATURE RANGE[1]

By A. B. Van Cleave[2] and O. Maass[3]

Abstract

The coefficients of viscosity of ammonia, propylene, ethylene and methyl ether, over the temperature range 23 to −80° C., have been measured. A comparison is made between the present data and those of other authors for temperatures above 0° C. It is estimated that the authors' results are correct to 0.2% and have a relative accuracy of 0.1%. It is claimed that they are the most accurate data for the viscosity of gases at low temperatures to date.

The validity of a number of viscosity–temperature relations has been tested with the present data and those previously published (18, 20). In general, it is found that the equations of Sutherland and Jones hold at high temperatures but fail at low temperatures for substances such as carbon dioxide, sulphur dioxide, ammonia, methyl ether and propylene, which have viscosity–temperature curves that are convex to the temperature axis below room temperature. An empirical equation is suggested which adequately represents the variation of viscosity with temperature for these five gases over the temperature range 23 to −80° C. However, this relation fails at high temperatures for all gases, and even at low temperatures for substances such as hydrogen, air and ethylene.

It is pointed out that the viscosity–temperature curves for carbon dioxide, sulphur dioxide, ammonia, methyl ether and propylene each show a definite inversion or inflexion point. Below this inversion temperature the viscosity curves are convex to the temperature axis; above it they are concave to the temperature axis. In general, it seems that this inversion temperature bears a direct relation to the polarity of the molecule and to the critical temperature.

Introduction

This research is a continuation of the systematic investigation of the viscosity of gases carried out in this laboratory. The object of the work is to obtain sufficiently accurate data to test rigidly certain proposed equations for the variation of the viscosity of gases with temperature, as well as to test the validity of an equation of state which depends on viscosity measurements (6, 12).

Owing to the failure of the classical kinetic theory of gases to represent adequately the variation of viscosity with temperature, a number of modified relations have been suggested. Sutherland (19) was the first to realize that the mean free path of a molecule must vary with the temperature and, in correcting for this factor, he derived his well known relation.

$$\eta = \eta_0 \left(\frac{T}{T_0}\right)^{\frac{1}{2}} \frac{T_0 + C}{T + C} , \tag{1}$$

where η is the coefficient of viscosity of a gas at the temperature T, η_0 is the viscosity of the gas at a standard temperature T_0, and C is a constant known as Sutherland's constant. This equation gave a fairly satisfactory representation of the variation of viscosity with temperature for a number of gases at high temperatures. However, the general failure of Sutherland's equation at low temperatures has been noted and discussed by Schmitt (15), Bestelmeyer (1) and Vogel (26).

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Chapman (4), in a detailed mathematical treatment of the dynamics of an encounter, derived expressions for the viscosity, diffusivity and thermal conductivity of a gas without assuming any property of the molecules save that they be spherically symmetrical. When his formula is applied to molecules acting as attracting spheres, Sutherland's equation is obtained. When molecules are considered as point centres of repulsive or attractive forces varying inversely as the n^{th} power of the distance the relation

$$\frac{\eta}{\eta_0} = \left(\frac{T}{T_0}\right)^n \tag{2}$$

results. Kamerlingh Onnes and Weber (11) found that Equation (2) gave a much better representation of the variation of the viscosity of helium over a large temperature range than did Equation (1).

Jones (10) developed a relation between viscosity and temperature on the basis that molecules repel according to an inverse n^{th} power law and attract according to an inverse third power law. His formula may be written

$$\eta = \eta_0 \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{T_0^{\frac{n-3}{n-1}} + S}{T^{\frac{n-3}{n-1}} + S} \quad , \tag{3}$$

where S is a constant depending on the index n of the repulsive field. For Maxwellian molecules n becomes infinite and Equation (3) reduces to Equation (1). For molecules acting as point centres of force the constant S becomes zero and Jones' equation reduces to the form of Equation (2). Hence, Jones' equation is more general than any yet given. This equation contains two adjustable constants, and hence it is not possible to determine either uniquely, as was noted by Jones (10). In general, he finds Equation (3) to conform to the experimental results better than Sutherland's equation.

Cooper and Maass (6) found that an empirical equation of the type

$$\frac{\eta}{\sqrt{T}} = a + bT \; , \tag{4}$$

(where a and b are constants), represented the data of Sutherland and Maass (20) for the viscosity of carbon dioxide over a low temperature range. Stewart (17) found Equation (4) to fit his results for the viscosity of sulphur dioxide at low temperatures. It is to be noted that Equation (4) could be considered as the expanded form of the exponential equation

$$\frac{\eta}{\sqrt{T}} = Ae^{BT} \; , \tag{5}$$

in which all but the first two terms in the converging series have been neglected.

The application of the above formulas to the data obtained in this work will be discussed later. It may be mentioned here, however, that up to the present there has been no wholly satisfactory, universally accepted formula for expressing the observed relation of viscosity and temperature—particularly at low temperatures. It is therefore desirable to extend accurate data in this direction.

Experimental

The apparatus was essentially the same as that used by Stewart and Maass (18) and described in detail by Sutherland and Maass (20). Since the publication of the results of the viscosity of sulphur dioxide by Stewart and Maass (18), an entirely new viscosity apparatus has been assembled and found to give results consistent with the previous determinations (18, 20). The only change that has been made in the original apparatus is the addition of two 4 in. reading lenses to facilitate the reading of the oscillating image. The lenses have been arranged so that they may easily be moved in a horizontal direction between the observer and the scale. They are set at the extreme ends of the scale at the beginning of an experiment and gradually moved towards the centre as the magnitude of the oscillations decreases. This arrangement makes the moving image much clearer and is a great aid to the eyes of the observer.

Preparation and Purification of Materials

Ammonia, propylene, ethylene and methyl ether were selected for this work on account of the ease with which they may be prepared and purified, and also because accurate data for their viscosities at low temperatures have not previously been given.

Ammonia was condensed from a tank of very pure anhydrous material and then fractionated twice at low temperatures before being distilled into the apparatus. The purity of the ammonia was indicated by the fact that it could easily be frozen when surrounded by a bath of solid carbon dioxide and acetone.

Propylene was prepared by the dehydration of isopropyl alcohol over alumina at 365° C., and was purified by low temperature fractionation as described by Maass and Wright (13). The fractionations were repeated until the vapor pressure was constant.

Ethylene was condensed from a tank of 99 9% pure material and then subjected to a series of low temperature fractionations in the apparatus used in the purification of propylene.

Methyl ether from a tank of 99.9% pure material was fractionated twice at low temperatures and then distilled into the viscosity apparatus. Magnetic stirring was used during fractionations.

The apparatus was filled with gas at room temperature after it had been thoroughly flushed several times with the pure material. At least half an hour was allowed for the gas to come to the temperature of the bath before any measurements were made. At temperatures below the normal boiling point of the gas used, the pressure was reduced so as to be well below the known vapor pressure at that temperature. Since it is known that the viscosity of a gas is independent of its pressure (20), the results obtained at low pressures are comparable with those obtained at atmospheric pressure.

The apparatus was calibrated with dry air free from carbon dioxide, as previously described (18, 20), both before and after a series of experiments in order to ensure that no change in the apparatus had taken place either during the course of the flushing with the pure gas or while the experiments were being made. The value of the wire constant used was that determined experimentally be Stewart (17).

Results

Table I shows the results obtained for the coefficient of viscosity of ammonia, methyl ether, ethylene and propylene. Each value is the mean of three or four independent experiments. These results are shown graphically in Fig. 1.

TABLE I

RESULTS OF MEASUREMENTS OF THE VISCOSITY OF AMMONIA, PROPYLENE, ETHYLENE, AND METHYL ETHER

Temp., °C.	$\eta \times 10^7$	Temp., °C.	$\eta \times 10^7$	Temp., °C.	$\eta \times 10^7$	Temp., °C.	$\eta \times 10^7$
Ammonia				*Propylene*			
24 27	1022.8	−26.70	825.6	24.16	858.3	−38.75	670.4
10.85	967 7	−47.02	755.5	18 69	840.6	−55.63	623.6
4 75	944.1	−57.65	719.4	9 36	813.3	−60.70	611.9
0.43	928.9	−71.25	675.2	0.00	784.1	−70.89	582.6
−12.30	878.7			− 0.15	783.9	−75.70	572.4
				−11.79	750.0	−79.72	561.5
				−25.84	709.3		
Ethylene				*Methyl ether*			
23.35	1010 6	−38.00	802.5	22.90	899.4	− 8.67	797.4
17.18	990.7	−52.50	752.3	18.11	883.0	−23.39	755.2
11.23	969.6	−60.38	724.2	11.71	862.4	−41.16	703.0
− 0.07	932.2	−68.52	697.2	−0 13	824.7	−56.91	658.4
− 9 02	900.8	−80.86	652.1				
−22.59	856.0						

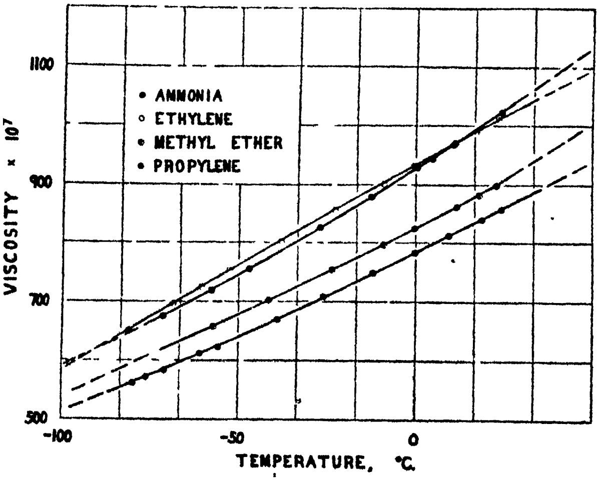

FIG. 1. *Variation of viscosity with temperature.*

Since measurements of the viscosity of gases at low temperatures are rare, comparisons between the present results and those of other authors can usually be made only at room temperature. Such comparisons are shown in Table II.

TABLE II

COMPARISON OF PRESENT RESULTS WITH THOSE OF PREVIOUS INVESTIGATORS

Gas	Temp., °C.	$\eta \times 10^7$			
		Observed in present work	Published previously		
Ammonia	25.1	1026	1002	Trautz and Heberling (22)	(1931)
	20.3	1007	982	Braune and Linke (2)	(1930)
	15.0	989	1005	Edwards and Worswick (7)	(1925)
	0.0	926	957	Graham (8)	(1849)
			918	Vogel (27)	(1914)
			950	Stackelbeck (16)	(1933)
	−77.1	656	680	Vogel (27)	(1914)
Propylene	20.0	845	835	Titani (21)	(1933)
	0.0	784	783	Titani (21)	(1933)
Ethylene	20.0	1000	1008	Trautz and Heberling (22)	(1931)
	0.0	932	966	Graham (8)	(1849)
			922	Obermayer (14)	(1875)
			961	Breitenbach (3)	(1901)
			907	Zimmer (29)	(1912)
			907	Titani (21)	(1933)
	−75.72	670	699	Zimmer (29)	(1912)
Methyl ether	20.0	889	1020	Graham (8)	(1849)
			910	Titani (21)	(1933)
	0.0	825	905	Graham (8)	(1849)
			850	Titani (21)	(1933)

Where there was no experimental value of viscosity for the temperature given by other authors, the observed values for the present work have been estimated from the curves in Fig. 1. Except for a few cases the agreement between the present results and those previously given is not good. The more recent data of Titani (21) and Trautz and Heberling (22) seem to be the most accurate. The present data for propylene and methyl ether check fairly well with those of Titani at room temperature. There is also good agreement between the authors' values and those of Trautz and Heberling (22) for ethylene. In the case of ammonia, however, agreement with these authors is not found. No doubt some of the discrepancies between the authors' values and those of the early workers in the field are due to the erroneous value for the viscosity of air assumed by them in their calculations. In Table II the results of Vogel (27) for the viscosity of ammonia have been corrected for this error.

Discussion

The present data, as well as those previously given (18, 20), will now be employed to test the validity of equations which represent the variation of viscosity with temperature.

It is interesting to make a comparison of Equations (1), (2), (4) and (5) for each of the gases for which low temperature data are available. The comparison over the approximate temperature range −80° to 30° C. has been made in the following manner. Experimental values of viscosity near the limits of the above-mentioned temperature range were selected and substituted in each of the four equations to obtain the values of the constants. With the constants thus determined the viscosity corresponding to some intermediate temperature, approximately in the centre of the temperature range, was calculated and compared with the experimental value. The results of these comparisons are summarized in Table III.

This summary shows that Equation (5) accurately represents the variation of viscosity with temperature in the temperature region in which the viscosity-temperature curve is convex to the temperature axis. In general, this seems to occur in the region well below the critical temperature. When the temperature–viscosity curve is concave to the temperature axis, Equation (5) fails entirely, whereas Equation (1) (Sutherland's equation) holds well over the temperature range selected. However, if a larger temperature range is selected Equation (1) also fails. In some cases Equation (2) might fit the results more accurately than Equation (1), *e.g.*, hydrogen in Table III.

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES

Gas	Deviation of equation, %			
	(1)	(2)	(4)	(5)
Carbon dioxide	2.57	1.43	0.88	0.18
Sulphur dioxide	1.67	0.94	0.30	0.21
Ammonia	1.77	1.35	0.82	0.21
Methyl ether	1.14	0.87	0.60	0.35
Propylene	1.48	0.94	0.32	0.20
Mean deviation	1.72	1.10	0.58	0.23
Ethylene	0.19	0.39	0.97	1.55
Hydrogen	0.33	0.21	0.60	0.72
Air	0.30	0.45	1.28	1.73
Mean deviation	0.27	0.35	0.95	1.33

In testing Jones' relation (Equation (3)), very good agreement between calculated and observed values is obtained in temperature regions where the viscosity curve is concave to the temperature axis. However, this equation, like Sutherland's, fails completely at low temperatures for gases like carbon dioxide, sulphur dioxide, ammonia, methyl ether and propylene. From Table III it may be noted that Equation (5) gives much the best representation of the variation of viscosity with temperature for these gases over the low temperature range considered. Equation (5) may be written in the form:

$$\log\left(\frac{\eta}{\sqrt{T}}\right) = aT + b \; . \qquad (6)$$

Thus, if log $(\eta/\sqrt{T})$ is plotted against the temperature, a straight line of slope a and intercept b should be obtained. This has been done for each of the above-mentioned five gases, and all the experimental points fell on a straight line for temperatures between 20° and −80° C. Table IV shows the values of the constants a and b determined in this manner.

A comparison of the observed results and those calculated by means of Equation (6) with the constants given in Table IV, shows agreement to within 0.2%, over the temperature range 30° to −80° C. However, this relation fails at the higher temperatures at which the relations of Sutherland and Jones have been found to hold. In general, Equation (5) or (6) seems adequate in temperature regions where the viscosity curve is convex to the temperature axis, as has been found for some gases at low temperatures.

TABLE IV

VALUES OF THE CONSTANTS OF EQUATION (6)

Gas		b
Carbon dioxide	0.000865	−5.32187
Sulphur dioxide	0.000855	−5.38600
Ammonia	0.001010	−5.52737
Methyl ether	0.000842	−5.53129
Propylene	0.000876	−5.56332

Since the viscosity of a gas does not vary directly as the square root of the temperature, owing to variation of the mean free path with temperature, Fig. 2, in which the quantity $\eta/\sqrt{T}$ for several gases is plotted against the temperature, graphically represents the variation of mean free path with

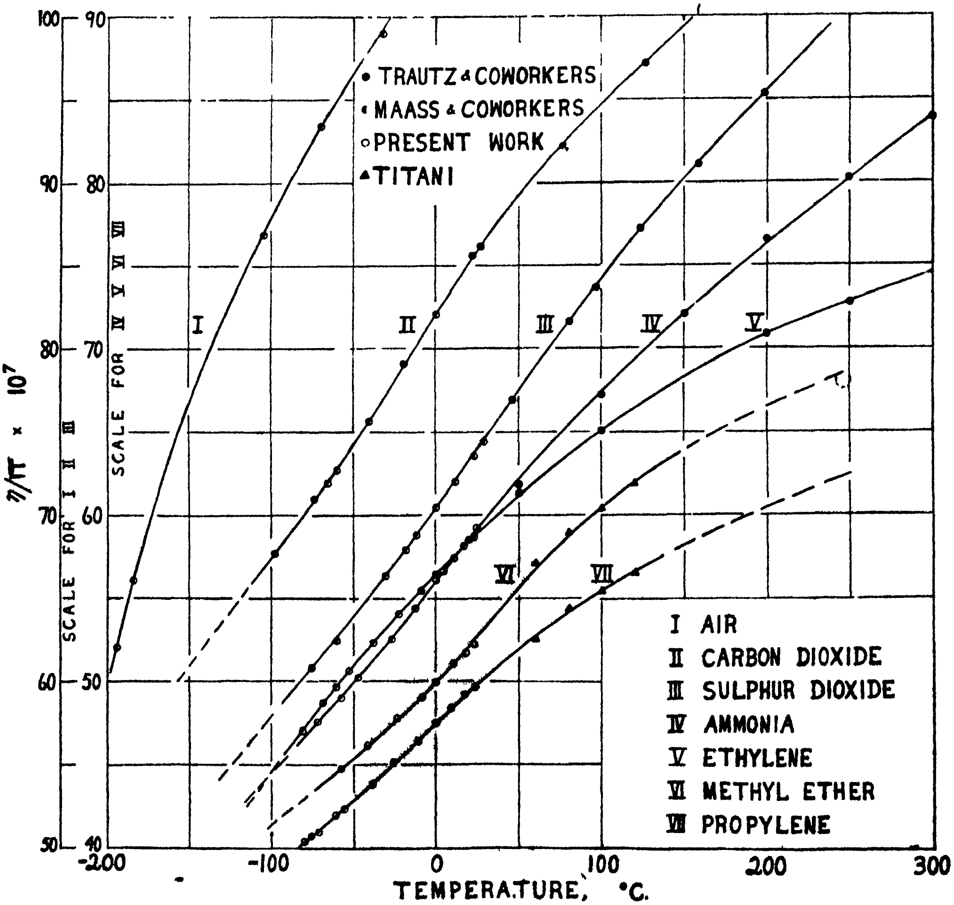

FIG. 2. *Variation of mean free path with temperature.*

temperature. For points above room temperature the data of Trautz and co-workers (22–25) for carbon dioxide, sulphur dioxide, ammonia and ethylene were used. The high-temperature values for methyl ether and propylene are those given by Titani (21). The low-temperature data for air and carbon dioxide are those given by Sutherland and Maass (20), for sulphur dioxide, those of Stewart and Maass (18). The low-temperature values for ammonia, ethylene, methyl ether and propylene are from the present work. Since the authors' values for the viscosity of ammonia at room temperature do not check with those of Trautz and Heberling (22), the whole high-temperature portion of the ammonia curve has been given a vertical displacement to make it continuous.

The curves for carbon dioxide, sulphur dioxide, ammonia, methyl ether and propylene in Fig. 2 each show a point of inflection or an inversion point. Below these points the viscosity–temperature curves are convex to the temperature axis, while above they are concave. Below this inversion point the authors have found Equation (5) to represent the variation of viscosity with temperature adequately. Other authors have found Sutherland's equation to hold well for the higher temperatures.

Fig. 2 shows that the temperature–viscosity curves for air and ethylene are always concave to the temperature axis over the temperature range considered. Hydrogen gives a similar curve (20). The data for the viscosity of helium (9, p. 286) give a curve which is concave to the temperature axis over the entire range −258 to 100° C.

So far as the authors know, the inversion from concave to convex at low temperatures in the viscosity–temperature curves has not been previously pointed out. The suggestion is made that this is the general form of the curve, and that if measurements could be made at low enough temperatures, air, hydrogen and ethylene would show similar inflections.

In general, it seems that the inversion point in the viscosity curves may be related to the critical temperature and the dipole moment of the gas. The approximate inversion temperatures for five gases in Fig. 2 have been found in the following manner. Starting with a temperature of −80° C., the value of $\eta/\sqrt{T}$ corresponding to every 10 degree rise in temperature was read off from the graphs for each gas. The increase in the value of $\eta/\sqrt{T}$ every 30 degree interval, , −80° to −50° C., −70° −40° C., etc., was found subtraction. These differences were then plotted against the mean tempera-

TABLE V

COMPARISON OF DIPOLE MOMENTS, CRITICAL TEMPERATURES AND INVERSION TEMPERATURES

Gas	Dipole moment $\mu \times 10^{18}$	Critical temp., °C.	Inversion temp., °C.
Hydrogen	0.00	−239.9	—
Air	0.00	−140.7	—
Ethylene	0.00	9.7	—
Carbon dioxide	0.13	31.1	12
Propylene	0.34	92.3	30
Methyl ether	1.32	126.9	42
Ammonia	1.48	132.4	35
Sulphur dioxide	1.66	157.2	65

ture of the interval. All the curves thus obtained showed a well defined maximum which corresponds to the point of inflection of the $\eta/\sqrt{T}$ *versus* temperature curves. These results, together with the values for the critical temperature and dipole moment of each gas, are given in Table V.

The dipole moments of hydrogen, air, ethylene, carbon dioxide, ammonia and sulphur dioxide are the mean of several values given in Table IV, p. 40 of Debye's "Polar Molecules". The value for methyl ether is that given in Table II, p. 8 of Debye's "Dipole Moment and Chemical Structure"; that of propylene is given by Watson, Rao and Ramaswamy (28).

The critical temperature values are those given in International Critical Tables, Vol. 3, p. 248.

Table V shows that the dipole moments, critical temperatures and the inversion temperatures of the viscosity curves are roughly parallel. The values of the inversion temperatures given are estimated to be correct to ±10° C. The only misplacement seems to be ammonia, but, when it is remembered that the data of Trautz and Heberling (22) had to be changed to check with the present data for ammonia, it may be suggested that this is perhaps due to experimental error.

The fundamental analysis of Jones (10) was based on an equal attraction or repulsion in all directions. Though this condition is approached at high temperatures for polar molecules, it is conceivable that at a sufficiently low temperature this postulate ceases to express the facts. The more polar the molecule, the higher the temperature at which this would occur. It may be possible to extend the theory to take this into account.

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THE INFLUENCE OF THE PREHEATING OF WOOD IN WATER ON THE RATE OF DELIGNIFICATION BY SULPHITE LIQUOR[1]

By A. J. Corey[2] and O. Maass[3]

Abstract

The rate of delignification of wood chips has been measured and found to conform to the monomolecular relation, provided that the standard method of penetration developed in this laboratory is used(3). Pretreatment of the wood chips by heating in liquid water at 130° C. decreases the rate of delignification by subsequent cooking in sulphite liquor, and the rate no longer conforms to the monomolecular relation. Preheating of the wood to 130° C. in the absence of water does not influence the rate of subsequent delignification. The results indicate the advantage of reducing the time of cooking, and a tentative explanation has been offered regarding the mechanism involved.

A study has been made of the delignification rate in calcium bisulphite liquor of sprucewood chips which have been subjected to three different types of heat pretreatment:—(i) In an atmosphere of nitrogen; (ii) in distilled water; (iii) in toluene. Black spruce heartwood of density 0.33 was used, and the chip size was 3 × 10 × 20 mm. The wood contained 30.5% of lignin, as determined by the method of Potter and Ross.

Method 1. The wood sample was dried in an oven at 105° C. for 24 hr. and weighed in a closed receptacle. It was then transferred immediately to a distilling flask fitted with a rubber stopper, through which a glass tube extended to the bottom of the flask. This tube was connected to a nitrogen cylinder, and the side arm of the flask, to a suction pump. The flask was evacuated and nitrogen introduced, the process being repeated several times to ensure the complete displacement of the air by nitrogen. This precaution was taken to avoid oxidation of the wood. The flask was immersed in an oil bath at a temperature of 130° C., and heated for one to six hours.

Method 2. Wood samples of known weight were placed in a vacuum desiccator, and after the vessel had been evacuated distilled water was run in. Then by alternately evacuating and applying atmospheric pressure the chips were completely impregnated with water. The chips were then removed, placed in a bronze bomb of 200 cc. capacity containing distilled water, and heated in an oil bath at 130° C. for definite periods of time.

Method 3. Pretreatment with toluene was carried out in a similar manner, except that the chips were thoroughly dried at 105° C. before impregnation with toluene. After the heat pretreatment was completed, the chips were removed from the liquid, dried at 105°, and evacuated to remove the last traces of toluene.

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After the heat pretreatment the chips were left in contact with air long enough to ensure that the moisture contents were approximately the same in every case.

The cooking was carried out in a small cell of 60 cc. capacity, so designed that it could be evacuated, and pressures up to 10 atm. could be applied during the cooking period. Wood samples of approximately six grams were used in each experiment. The composition of the calcium bisulphite cooking liquor was as follows:—total SO_2, 5.15; free SO_2, 3.90; combined SO_2, 1.25%.

The cooking procedure was as follows. The chips were placed in the cell which was then subjected to evacuation for 30 min. at a pressure of one centimetre of mercury. The cooking liquor was run in, the cell immersed in the oil bath and the temperature raised to 140° C. in 30 min. The temperature was then held constant for the duration of the experiment by means of a suitable electric thermoregulator, and the pressure in the cell kept at seven atmospheres by means of a cylinder of compressed nitrogen gas and a reducing valve.

The chips were removed from the cell, disintegrated with a small, high speed electric disintegrator, and washed several times with distilled water. The resulting pulp was divided into two portions, one being used to make a test sheet, and the other for analytical determinations.

Experimental Results

In the first series of experiments (Table I, A) wood samples were heated in an atmosphere of nitrogen, as described in Method 1, for varying periods of time, and afterward were cooked at maximum temperature (140° C.) for three hours.

TABLE I

EFFECT ON COOKING PROPERTIES OF WOOD OF PREHEATING TO 130° C. IN *(A)* NITROGEN, AND IN *(B)* WATER

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %, based on wood used	Mullen strength, %	Time of pretreatment at 130° C., hr.
A. Method 1.—Preheating in an atmosphere of nitrogen						
110	53.2	49.3	7.35	3.9	166.5	No pretreatment
119	53.7	50.2	6.45	3.5	159.5	No pretreatment
122	55.7	52.1	6.42	3.58	157	1
115	54.4	51.1	7.11	3.86	150	2
117	53.0	49.2	7.22	3.92	175	4
121	53.8	50.2	6.74	3.63	164	6
B. Method 2.—Preheating in water						
111	54.8	48.8	11.0	6.2	132	1
113	58.2	51.0	12.4	7.23	109	2
116	65.0	54.6	16.1	10.45	54.0	4
120	67.5	54.0	20.05	13.5	—	6

The yield of cellulose was determined by difference, and so includes all carbohydrates not determined as lignin.

For purposes of comparison two runs were made on untreated wood chips.

Table I, *B*, shows the results obtained when the chips were pretreated by heating in water at 130° C. for varying periods of time, and then cooked for three hours at 140° C.

Table II is a comparison between wood heated in toluene at 130° C. for six hours, and untreated wood. The two samples were cooked for three hours at 140° C.

TABLE II

RESULTS OBTAINED WITH WOOD PRETREATED IN TOLUENE AND WITH WOOD NOT PRETREATED

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Mullen strength, %	Type of treatment
134	52.2	48.8	6.88	3.6	145	Toluene-treated
110	53.2	49.3	7.35	3.9	166.5	Not pretreated

The runs listed in Table III were made on chips which had been pretreated in water for six hours at 130° C. and then cooked at 140° C. for the periods of time indicated.

For purposes of comparison a "burnt cook" was obtained as follows. Untreated chips were placed in the cooking cell and the usual pre-evacuation

TABLE III

RESULTS OBTAINED WITH WOOD PRETREATED FOR SIX HOURS WITH WATER AT 130° C., AND WITH UNTREATED WOOD

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Mullen strength, %	Hours cooked at 140° C.
A. Chips pretreated for six hours in water at 130° C.						
123	43.3	42.4	1.83	0.79	100	8
129	45.2	44.3	2.08	0.94	130	7
127	47.0	45.4	3.35	1.57	130	6
126	50.5	47.2	6.62	3.34	138	5
128	59.3	52.0	12.3	7.3	63.5	4
120	67.5	54.0	20.05	13.6	—	3
132	80.7	60.0	25.2	20.3	—	1.5
B. Untreated wood						
135	46.3	45.0	2.55	1.17	145	5
110	53.2	49.3	7.35	3.9	166.5	3
131	65.3	55.8	14.4	9.4	—	1.5
130	85.9	61.3	28.7	24.7	—	0.5

was omitted. The liquor was introduced and the cell immersed in the oil bath, which had been preheated to 120° C. The temperature of the bath was raised to 140° C. in 15 min.

A three hour test run was made and definite "burning" was obtained. Using the same procedure, Run 125 was "burned" at the beginning and the cooking continued for eight hours.

TABLE IV

RESULTS OBTAINED WITH A BURNT COOK

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Mullen strength, %	Length of cook, hr.
125	43.5	37.5	13.5	5.8	—	8

Discussion

A consideration of Table I, *A*, shows that the cooking properties of wood are not altered by heating to 130° in the absence of liquids. Any variation in the results, particularly in the mullen strength, is to be attributed to variations in the composition of the different samples. Small knots in the dry wood chips are hard to detect and wood containing them will yield a sheet containing shives. Hence the mullen strength value is lowered.

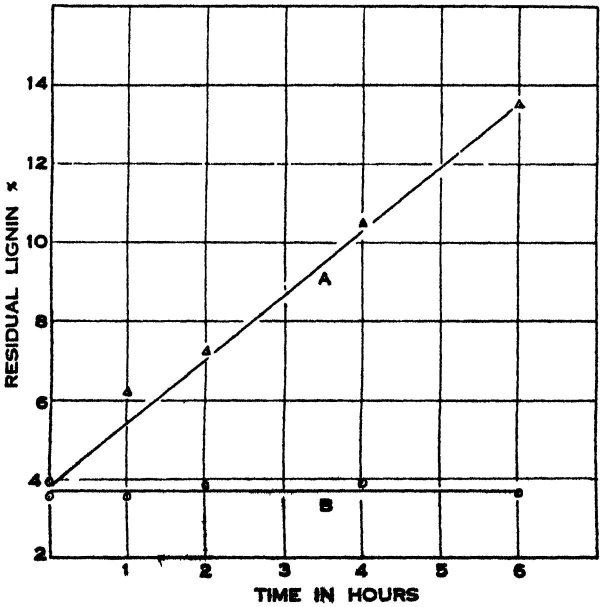

FIG. 1. *Influence of preheating wood at 130° C. on delignification in a 3 hr. standard sulphite cook at 140°* (*A, pretreated by Method 2; B, pretreated by Method 1.*

Table I, *B*, indicates that heat treatment of wood in water makes subsequent delignification of the wood in calcium bisulphite liquor very difficult, and this effect increases with the length of the pretreatment. The wood pretreated for six hours was so slightly cooked after three hours at 140° C. that the chips could not be disintegrated.

The difference in the results obtained by the two methods of pretreatment is brought out in Fig. 1, in which the residual lignin, calculated on the basis of the original wood, is plotted against the time of pretreatment.

In order to ascertain whether liquids other than water produced this effect, a wood sample was pretreated in toluene for six hours at 130° and cooked for three hours at 140° C. In Table II the results of this run are compared with those of a cook made on untreated wood, also cooked three hours.

Table III, *A*, shows that wood pretreated in water can be delignified if cooked a sufficient length of time, but owing to this increased period of digestion the cellulose fibres are degraded and low mullen strengths are obtained. The maximum strength is shown after five hours' cooking but with untreated wood (Table III, *B*) the maximum strength is indicated after three hours' digestion.

The results of Run 125 confirm the belief that a "burned cook" cannot be delignified by prolonged cooking. The rate of cellulose degradation was more rapid in this case than the rate of delignification, so that no separation of cellulose from lignin could be obtained. It would then appear that the result of water-heat pretreatment differs in nature from that of "burning".

Investigation has shown that the rate of delignification in the sulphite process approximates that given by a monomolecular reaction (4, 5) *i.e.*,

$$\frac{1}{t}\ln\frac{L_0}{L} = k,$$

where t is the time in hours, L_0 the percentage lignin in the wood, L the percentage lignin remaining at time t, and k the velocity constant of the reaction. Thus if the logarithm of the percentage of residual lignin, calculated on the weight of the wood, is plotted against time, a straight line relation should be obtained. This result has been obtained with woodmeal in a thorough investigation carried out by Yorston (5). The authors found that the same result could be obtained with wood chips provided that the perfect penetration procedure outlined by de Montigny and Maass (1) was followed.

In Fig. 2 are plotted values taken from Table III, and though the untreated wood follows the monomolecular relation approximately, the pretreated wood shows a great deviation.

According to Hägglund (2) there are three main reactions leading to the removal of lignin—

1. Sulphite addition to the lignin-carbohydrate compound in the solid phase.
2. Hydrolysis of the lignin sulphonic carbohydrate compound in the solid phase.

3. Hydrolysis of the liberated carbohydrate. Sulphur determinations made in the experiments listed in Table III, *A*, indicated that sufficient sulphonation had taken place, so that the decreased rate of delignification observed with pretreated wood must be attributed to a change in the rate of hydrolysis. A possible explanation is advanced to account for this change, and for the shape of the curves in Fig. 2.

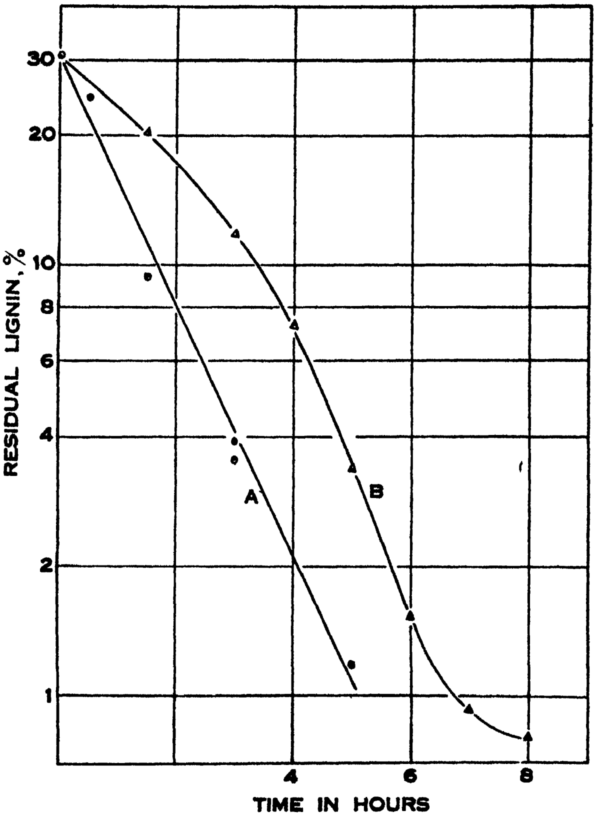

FIG. 2. *Rate of delignification of untreated and of preheated wood. A, untreated wood, B, pretreated by Method 2.*

If the lignin is present in the wood as submicroscopic particles, heating in aqueous solutions might tend to cause agglomeration and increase in particle size. On the other hand, the cooking action tends to decrease the particle size, so that in the cooking process two opposite effects are superimposed. If these two effects could be separated, curves would be obtained as shown in Fig. 3, but acting together the two cancel and give the straight line relation required by the monomolecular rate.

When wood is pretreated by heating in water the particle size of the lignin is increased to a maximum, and the rate of delignification greatly decreased in the first stages of the process. Later on, the effect of decreasing particle size, brought about by the cooking action, predominates and the curve falls rapidly.

The inflexion in the curve after seven hours may indicate that some of the lignin is more resistant to removal, but the inaccuracy of lignin determinations in this region of the curve makes it of doubtful significance.

This work was repeated using a wood specimen of different density, and the same results as those described above were obtained. They have been omitted owing to lack of space.

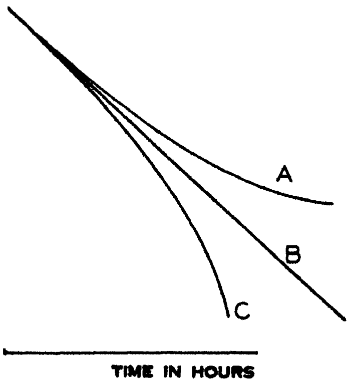

FIG. 3. *Effect of changing particle size on the rate of delignification. A, effect of increasing particle size; B, monomolecular relation, C, effect of decreasing particle size.*

The hypothesis advanced to explain the effect of heat pretreatment in water is of course a tentative one, and other explanations, such as a structural change in the lignin, produced by the pretreatment, suggest themselves. In any case it appears from the experiments described that a decrease in cooking time will benefit the process of delignification, an additional reason for finding means of decreasing the so-called penetration period. Experiments designed to test this out are contemplated. Furthermore work is being undertaken on the pretreatment of wood in aqueous solutions of salts, acids, and bases, but sufficient results have not yet been obtained to warrant the drawing of conclusions.

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MEASUREMENT OF THE VARIATION OF THE DIELECTRIC CONSTANT OF WATER WITH EXTENT OF ADSORPTION[1]

By G. H. Argue[2] and O. Maass[3]

Abstract

An experimental technique has been devised for the measurement of the dielectric constants of cellulosic materials containing various amounts of adsorbed water. From measurements made with standard cellulose the dielectric constant of the adsorbed water was calculated over the concentration range 0 to 18% of water. The dielectric constant of the water initially adsorbed is less than one-quarter of that of liquid water, but it increases with the amount of water subsequently adsorbed, until the dielectric constant approximates that of liquid water as the water content of the fibre approaches the saturation point. These results are shown to be in agreement with the hypothesis concerning the nature of the system cellulose–water.

Introduction

In a recent paper (1) the nature of the adsorption of water on cellulosic materials was discussed at considerable length. With the hope of finding further evidence in favor of the views set forth, an investigation was started in which the change in the dielectric constant of the adsorbed water with increasing concentration of water was measured. A technique was developed whereby the dielectric constant of bone-dry cellulose could be determined and subsequent measurements made after the addition of a known amount of water.

While no work has been published on the dielectric constant of water adsorbed on cellulose, a paper by Von Tausz and Rumm (5) on the dielectric constant of adsorbed water appeared while this work was in progress. The sorbents used by them were silica, lignite and tobacco. Of these, only the last-named bears any similarity to the system to be described. Their results will be discussed later.

Apparatus

The dielectric constant apparatus that was employed has been in use in this laboratory for some time. With it, small capacities are measured by means of a heterodyne beat method. The set-up was arranged to give a wave-length of 600 metres. The frequency of the two oscillators differed by 1000 cycles per sec., so that a telephone could be used for the null point reading. The precision-measuring condenser was mounted in the centre of a circular platform, 5 ft. in diameter, with a 6 in. vertical scale around the edge. A beam of light was thrown on a small mirror fastened to the central rotor shaft of the condenser so that a spot of light was reflected on to the scale. The sensitivity was such that a change of 0.05 cm. on the scale could be easily detected.

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The experimental condenser consisted of two concentric brass cylinders 0.07 cm. in thickness. The inner diameter of the larger cylinder was 2.58 cm., and the outer diameter of the smaller plate was 2.05 cm. The outer and the inner condenser plates were respectively 22.95 cm. and 23.6 cm. in length; the entire condenser was enclosed in a glass tube provided with platinum leads and an outlet to the evacuated glass system, as shown in Fig. 1. The outer brass plate fitted snugly into the glass cylinder and three small prongs on each plate held the condenser centrally in the glass tube. The dimensions of these projections were: on inner cylinder, 2 by 0 29 by 0.07 cm.; on outer cylinder, 1.02 by 0 4 by 0.07 cm. A direct electrical contact was made between the platinum wires and two of the outer binding posts of a double-throw mercury switch, not shown in the diagram. The central binding posts were connected to the capacity-measuring apparatus. With the switch in one position the capacity of the external leads from the measuring condenser to the mercury switch was measured. With the switch in the other position, the total capacity of the external leads, internal leads from the switch to the condenser plates and the experimental condenser itself was determined. The experimental capacity readings given in this work are the differences in the capacities measured when this switch was in these two positions. That is, the measured capacity was due to the brass condenser and its internal leads only. Further, the repeated measurement of the capacity of the external leads served as a check on the operation of the capacity-measuring apparatus.

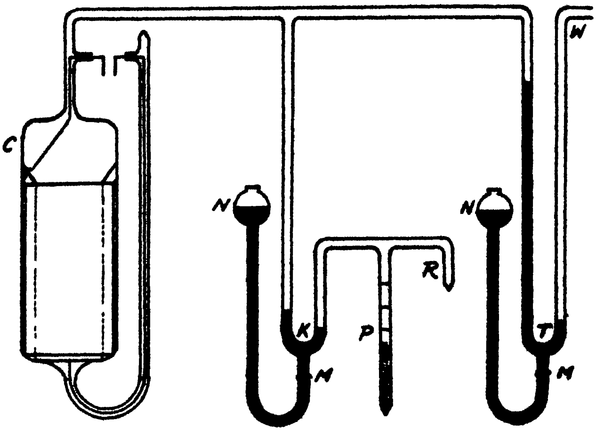

FIG. 1. *Apparatus for measuring dielectric constants of water adsorbed on cellulose.*

All external leads were enclosed in copper tubes which were held in a fixed position and earthed. The various parts of the entire capacity-measuring apparatus were grounded. Further, the oil bath surrounding the experimental condenser was provided with a constant level device, so that no variable capacity effects due to a change in the volume of liquid in the bath were introduced. The metallic parts of the thermostat and the supports for the glass apparatus were connected to an equipotential, earthed shield. The negative side of the 110 volt d-c. which supplied the power for the motor and heaters was grounded through a 10,000 ohm resistance. It was found that the effect of mutual and earth capacity had been minimized, and since only differential capacity measurements were made, any small variable change in capacity cancelled out, or was negligible compared to the large capacity of the experimental condenser.

The evacuated glass system, shown diagrammatically in Fig. 1, was of simple design. Two mercury traps *T* and *K* were used in place of stopcocks. The former served as a manometer by which the pressure in the apparatus was measured; it also formed a seal between the entire apparatus and the atmosphere. The latter isolated the short section forming the pipette, *P*, by which the amount of water vapor admitted to the chamber containing the cellulose was measured. By adjusting the leveling bulb, *N*, and the stopcock, *M*, the required amount of water could thus be admitted. The pressure in the entire system could be reduced to that of 10^{-5} cm. of mercury in a few minutes by means of the two mercury diffusion pumps and a Cenco Hyvac pump, all in series and sealed on at *W*. In order to ensure that water vapor did not condense in the various parts of the apparatus when the moisture content of the cellulose sample approached the saturation point, two precautions were taken. Fine resistance wire (16 ohms per foot) was wound around the glass tubing connecting the component parts of the system, and a small current was passed through the wire. In this way the temperature of the glass was maintained at from 30 to 35° C. Further, a small Dewar flask filled with ice was placed around the pipette before the water level was measured.

Experimental Procedure

A weighed sample of dry cellulose, purified as previously described (1), was packed into the annular space between the plates of the experimental condenser. The apparatus was assembled in the glass case, *C*, and the electrical contacts were made.

A small bulb, partly filled with distilled water, was sealed to the system at *R*, and small traces of gas were removed by alternate freezing and melting of the liquid while the apparatus was kept evacuated. The part of the system forming the pipette was shut off from the remainder of the apparatus by the mercury in the trap *K*, and the liquid was distilled into the pipette and the bulb was sealed off at *R*.

In order to remove the water vapor which the cellulose sample sorbed from the atmosphere during its transfer to the condenser, the temperature of the oil bath was raised to 100° C. and maintained at that point for two hours. The entire apparatus was evacuated and at regular intervals dry air was admitted to the system until the pressure was approximately that of 20 cm. of mercury, and allowed to remain in contact with the sample for 10 min. Finally, the bath was cooled to 25° C., the temperature control was regulated and the mercury limb in the manometer *T* was raised to a height sufficient to withstand atmospheric pressure.

The capacity of the condenser containing dry cellulose was measured. A known volume of water was allowed to evaporate into the evacuated system by lowering the level of the mercury in *K*. After equilibrium was established, the capacity of the condenser was again determined. This procedure was repeated until the fibre was almost saturated. Furthermore, the difference between the barometric pressure and that indicated by the height of the mercury in the manometer *T* was the equilibrium pressure of the water vapor in contact with the cellulose. By means of the vapor pressure-adsorption data (5), it was possible to check the amount of water adsorbed on the sample, and also to ensure that equilibrium was established before the capacity was measured.

Capacities could be measured to within 0.1%. For a sample containing up to 2% of adsorbed water the change in the capacity was 2.3 cm. units. At this concentration the probable error in the value deduced for the capacity of water was 1.6%. When the water concentration on the cellulose sample was 10%, the probable error was 0.3%, and with the higher moisture concentrations the errors were smaller.

The largest probable error was introduced by the measurement of the amount of water adsorbed by the cellulose. The volume of water was estimated to within 0 005 cc.; the total volume of water adsorbed by cellulose containing 2% of water was 0.1 cc., hence the probable error was 5%. The error decreases and, with increasing amounts of water, eventually becomes less than 1%.

The Calculation of the Dielectric Constant

The absolute value of the capacity of the condenser was measured and it agreed fairly well with that calculated on the basis of the dimensions of the condenser. The difference between the calculated and the measured capacity of the condenser can be accounted for by certain lead corrections and the capacity due to the projections on the top of the condenser. These corrections were difficult to estimate. Since it was found that the actual capacity of the condenser does not enter into the calculation of the dielectric constant of the absorbed water, this difference will not be considered further.

The capacity of the empty condenser is given by the following relation:

$$L + C = xd_1,$$

where L is the capacity due to the internal lead wires from the condenser plates to the mercury switch, C is the capacity of the condenser, d_1 is the measured deflection on the scale of the measuring condenser, and x is a proportionality factor, which can be calculated from a consideration of the calibration of the measuring condenser by the measurement of the capacity of a standardized fixed capacity.

Similarly, the capacity of the internal leads is

$$L = xd_2.$$

At the conclusion of the experiments the glass tube surrounding the condenser was opened, the two cylindrical plates were removed, and the capacity of the internal leads was measured. The lead wires were in the same position relative to one another as they were in the actual experiments. Hence, d_2 is the deflection on the scale of the measuring condenser due to the capacity of the lead wires. The value of d_2 found experimentally was 8.0 cm. From these two relations, it follows that the capacity of the condenser is given by

$$C = x(d_1 - d_2).$$

Further, the capacity of the condenser filled with dry cellulose, C_m, is

$$C_m = x(d_3 - d_2),$$

where d_3 is the deflection measured by the precision condenser.

The dielectric constant of the cellulose-air mixture, ϵ_m, will be given by

$$\epsilon_m = \frac{(d_3 - d_2)}{(d_1 - d_2)}.$$

From the last equation, the value of ϵ_m was calculated as follows

$$\epsilon_m = \frac{82\ 96 - 8\ 0}{68\ 23 - 8\ 0} = 1.24.$$

Hence the dielectric constants of the cellulose and of the adsorbed water do not depend on the absolute capacity of the condenser, since they are calculated from the dielectric constants of the cellulose-air and cellulose-air-water mixtures given by the above relation.

Also, it should be pointed out that the method used and the arrangement of the electrical measuring apparatus were such that the electrical conductivity of the adsorbed water had no effect on the results of the capacity measurements. This method was, in part, developed in this laboratory for the measurement of the dielectric constant of water and hydrogen peroxide (4).

It is difficult to estimate the dielectric constant of a dielectric that does not completely fill the space between the plates of the condenser. If the sample is in a regular arrangement in layers parallel to the surface of the plates with air spaces between the layers, it can be shown that

$$\epsilon_m = \frac{1}{\frac{v_1}{V} + \frac{v_2}{V\epsilon}}, \tag{1}$$

where ϵ is the dielectric constant of the substance, ϵ_m is the resultant dielectric constant of the material and the air in the sample, and $\frac{v_1}{V}$ and $\frac{v_2}{V}$ are the volume percentages of air and the substance.

If the dielectric is arranged at right angles to the surface of the plates, that is, if the material forms a continuous conductor across the air gap between the plates with alternate columns of air and material, it can be shown that—

$$\epsilon_m = \frac{v_1}{V} + \frac{v_2}{V}\epsilon. \tag{2}$$

According to Lichtenecker (3), if the dielectric is in the form of very small particles distributed at random in the air space in the condenser, the following empirical relation obtains

$$\log \epsilon_m = \frac{v_2}{V} \log \epsilon \ . \tag{3}$$

The diagrams shown in Fig. 2, clearly define the spatial arrangement of the dielectrics in the mixture between the plates. In Fig. 2, *a*, *b* and *c* refer to Relations 1, 2, and 3, respectively.

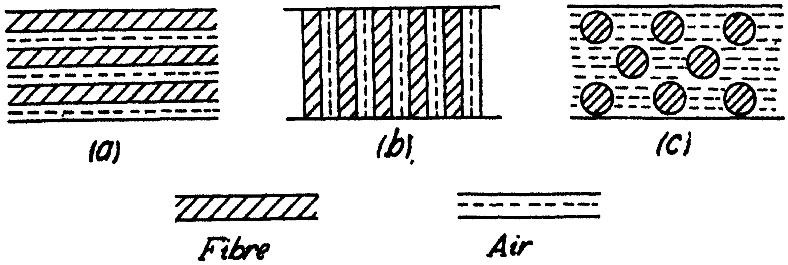

FIG. 2. *Diagrammatic representation of typical distributions of dielectric and air in condenser.*

For the measurement of the dielectric constant of cellulose from the capacity measurements of a condenser filled with cellulose fibre, it is obvious that the first relation cannot be applied. It might appear that the relation between ϵ_m and ϵ given in Equation (3), would be the correct one. However, cellulose consists of fibres, the average length of which is 2.5 cm., while the distance between the plates of the experimental condenser used in this work was 0.265 cm. Also, from the manner in which the cellulose was packed into the condenser, it is probable that the second relation is the one most closely approximated.

From the dielectric constant of the mixture of dry cellulose and air in the condenser (as calculated above), it is possible to determine the dielectric constant of cellulose by means of Equation (2). The volume percentages of dry cellulose and air are 7.87 and 92.13%. Hence, the dielectric constant of cellulose, ϵ, is

$$1\ 24 = 0\ 921 + 0\ 079\epsilon$$
$$\epsilon = 4\ 11$$

Similarly, from Equation (3)

$$\log 1\ 24 = 0\ 079 \log \epsilon$$
$$\epsilon = 13\ 21$$

There is no generally accepted value for the dielectric constant of cellulose. It is pointed out in The International Critical Tables (2) that the value of ϵ is between 3.9 and 7.5. It is improbable that the dielectric constant of cellulose is 13, as given by Equation (3). That of a carbohydrate such as sugar is 4. Hence, it would appear that Equation (2) gives for the dielectric constant of bone-dry cellulose a value that is of the right order of magnitude. As the main interest in the subsequent work lies in the relative values to be assigned to the dielectric constant of the adsorbed water, and as the experiments were carried out in such a way that the position of the cellulose fibres was not altered by the adsorption of the water vapor, whatever arrangement of the cellulose fibres holds for the calculation of the dielectric constant of dry cellulose also holds for the subsequent calculation of the dielectric constant of the adsorbed water. Since Equation (2) gives a reasonable value for the dielectric constant of cellulose, this relation will be used in the calculation in connection with the adsorbed water. It can be expected that the relation of any one value of the dielectric constant of adsorbed water to another is correct.

In the use of Equation (2), extended to include the system cellulose–air–water, it was assumed that during adsorption the volume of the water remained unchanged. It has been shown that a contraction in volume of the adsorbed water takes place. Even if this contraction is as large as that found by Filby and Maass, it was not assumed by them that the water alone suffered this contraction. Part of the decrease in volume will undoubtedly be participated in by the cellulose. Thus, the true volume of the water is an unknown quantity, and was not taken into account. Later on, this will be referred to again, as the values for the dielectric constant of adsorbed water show that some such contraction in the system does take place when adsorption begins.

Results

The experimental data and the calculated values of the dielectric constant are given in Table I. The true weight of water sorbed on the sample, corrected for the amount of water vapor in the total evacuated volume of the

TABLE I
CALCULATED DIELECTRIC CONSTANTS

Weight of water sorbed, gm.	Gm., H_2O/gm. cellulose	True capacity, cm.-units	Dielectric constant of mixture	Dielectric constant of adsorbed water
Run 1				
0.0	0.0	74.73	1.241	—
0.096	0.0189	77.01	1.279	15.73
0.438	0.0862	90.60	1.504	25.48
0.792	0.156	119.0	1.976	39.22
Run 2				
0.0	0.0	74.96	1.245	—
0.037	0.0073	75.58	1.255	12.81
0.117	0.0230	77.63	1.289	16.70
0.230	0.0452	81.61	1.355	20.84
0.343	0.0675	86.28	1.433	23.63
0.453	0.089	90.74	1.507	24.91
0.611	0.120	103.85	1.724	33.46
0.840	0.165	122.0	2.026	39.51
0.0	0.0	75.10	1.247	—

apparatus, is shown in the first column. Knowing the weight of the sample, 5.084 gm., it was possible to calculate the weight of water adsorbed per gram of dry cellulose. The third column shows the true capacity of the condenser and its contents, in units of the scale divisions of the measuring condenser, when the water concentrations are those shown in the preceding columns. The dielectric constants of the heterogeneous system cellulose–air–water are shown in Column 4. These data, shown in Fig. 3, were calculated as mentioned previously. The dielectric constant of the mixture, ϵ_m, increases as the volume of water adsorbed becomes larger. In the last column the dielectric constant of the adsorbed water, calculated from an extended relation similar to that given by Equation (2), is shown. A typical example follows:—

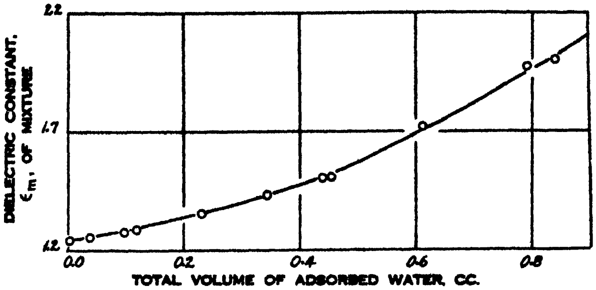

FIG. 3. *Relation between dielectric constant of mixture cellulose–water and air and water content of cellulose.*

Total volume of the condenser, 41.4 cc.; weight of cellulose, 5.084 gm.; volume of cellulose = 5.084 × 0.62 = 3.26 cc.; volume of water, 0.23 cc.; volume of air = 41.4 − 3.26 − 0.23 = 37.91 cc.; dielectric constant of air, 1; dielectric constant of cellulose, 4.11; dielectric constant of the mixture, 1.35. Hence,

$$1.35 \times 1 = 1 \times \frac{37.91}{41.4} + 4.11 \times \frac{3.26}{41.4} + \epsilon_{H_2O} \times \frac{0.23}{41.4}$$

$$\epsilon_{H_2O} = 20.84.$$

The dielectric constant of 0.23 gm. of adsorbed water is 20.84. The data in Column 5 are shown graphically in Fig. 4. An inflection in the curve occurs at a point corresponding to a water content of approximately 0.09 gm. of water per gram of dry cellulose. This apparent discontinuity may be explained in the following manner.

If the water first adsorbed on the cellulose surface occupies a smaller volume than is accounted for if a density of 1 gram per cc. is assigned to it, then the dielectric constant of the adsorbed water as calculated is too small. In the range of small water contents, the curve might well take the form shown by the dotted line, if the volume contraction of the adsorbed water could be taken into account.

The values of the dielectric constant shown in the last column of Table I are the mean dielectric constants of the adsorbed water over the concentration range from the concentration corresponding to zero adsorption to that at which the measurement was made. It is possible to calculate the dielectric constant of a small volume of water that would increase the water content concentration over a small range. The additive relation expressed by Equation (2) may be given in the form—

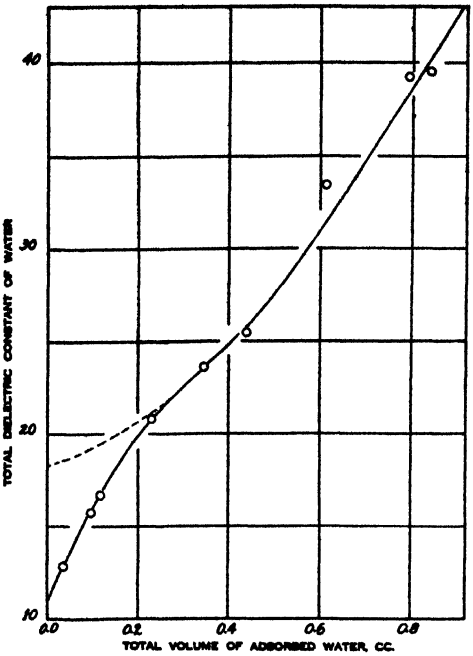

FIG. 4. *Relation between dielectric constant of all water adsorbed on cellulose and amount of water adsorbed.*

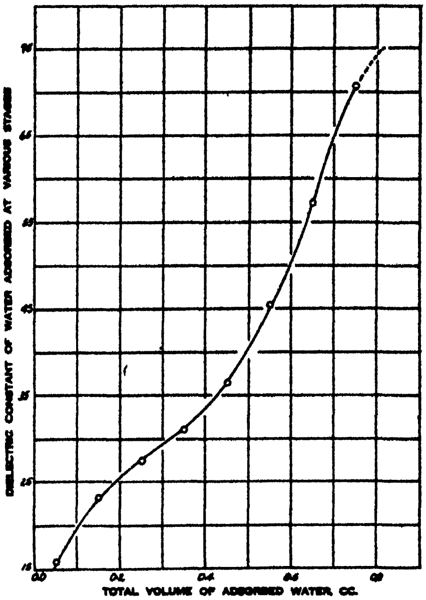

FIG. 5. *Relation between dielectric constant of water adsorbed at various stages and volume of adsorbed water.*

$$\epsilon_{v_2} \times v_2 - \epsilon_{v_1} \times v_1 = \epsilon_{(v_2 - v_1)},$$

where ϵ_{v_1} and ϵ_{v_2} are the dielectric constants when the volumes of sorbed water are v_1 and v_2 respectively, and ϵ is the dielectric constant of the small increment of water. In Table II the value of ϵ for each increment of water is given.

TABLE II

AVERAGE DIELECTRIC CONSTANT OF WATER ADSORBED OVER A SMALL CONCENTRATION RANGE

Range of water content, $V_2 - V_1$, (cc.)	Dielectric constant of water added	Range of water content, $V_2 - V_1$, (cc.)	Dielectric constant of water added
0.0–0.1	15 8	0.4–0.5	36 5
0.1–0 2	23 6	0.5–0 6	45 5
0.2–0.3	27.5	0.6–0.7	57.3
0 3–0 4	31.1	0 7–0.8	70.7

In Fig. 5 the average dielectric constant for each definite volume of water, 0.1 cc., adsorbed by the cellulose over the concentration ranges shown in Table II, is plotted against the mean volume of water present on the cellulose between these concentration limits.

When the concentration is 0.8 cc. of adsorbed water, 16% adsorption, the cellulose sample has sorbed an amount of water that is just 4% lower than that found at the fibre saturation point. The last portion of water adsorbed might be expected to be mainly in capillary tubes. Such adsorbed water would have a dielectric constant of 79, so that the dielectric constant of the adsorbed water apparently approaches that of liquid water.

Discussion of Results

Since the value for the dielectric constant of cellulose is a reasonable one and that of the adsorbed water near the fibre saturation point agrees with the accepted value for the dielectric constant of water, all the indicated values of the dielectric constants of water probably do not differ much from the true values. The relation used in the calculation would give too small a value, since only a part of the cellulose fibres are in pillar formation. However, the lines of force would be drawn in to a certain extent if the dielectric is spread in pillar formation, and the relation in Equation (2) would give too high a value for the dielectric constant of the mixture. It may be that the cellulose spread laterally just compensates for this effect and that the results found are, therefore, very nearly the absolute ones.

However, no emphasis is laid on the foregoing fact, as it may be entirely fortuitous, and the value of the dielectric constant of cellulose may well be higher than that given by Equation (2), namely, 4.11.

The main object of this investigation has been achieved independently of the accuracy of the absolute values. It has been shown that the dielectric constant of the adsorbed water becomes larger with increased adsorption, gradually reaching the value for liquid water.

Von Tausz and Rumm (5) found that the dielectric constant of water adsorbed on tobacco decreased from 90 to 25, when the water content was reduced from 19 to 15%. A change of this magnitude is improbable. The dielectric constant of water at 25° C. is actually less than 90 (4). The 4% change that occurs in water concentration in the vicinity of the fibre saturation point will not change the nature of the adsorbed water to so appreciable an extent. The relation that these experimenters used, Equation (3), while probably legitimate for their measurements with powders, is not so when applied to a fibrous material, which on packing spreads, to some extent, from one electrode to the other.

Conclusion

The large value of the dielectric constant of a polar liquid is due mainly to the orientation that the liquid molecules, which are free to rotate, assume in an electric field. Adsorbed molecules will not have the freedom that those in the liquid have. The water molecules that form the first adsorbed layer on the cellulose micelle will be strongly held to the surface and will rotate through only a very limited range. The dielectric constant of these adsorbed water molecules would be low. The molecules in a second adsorbed layer would not be as securely anchored, and would be free to rotate through a larger range under the influence of an electric field. Hence, the dielectric constant of the adsorbed water increases with further additions. At a point in the water adsorption where the adsorbed molecules are no longer under the influence of the surface, the dielectric constant of the adsorbed water would reach a maximum value equal to that of liquid water. That the dielectric constant does not increase abruptly to its limiting value as soon as the initial free surface has been saturated is to be expected. New surface for water adsorption is created continuously as further amounts of water are adsorbed. This fact is shown clearly in Fig. 5. The experimental results are, therefore, an excellent confirmation of the hypothesis regarding the physical structure of cellulose, and the mechanism of adsorption that was given in the introduction.

From the forms of the various graphs, one is tempted to draw quantitative conclusions regarding the amount of water which is adsorbed, the amount held as liquid water, and the amount of new cellulose surface created in the various stages of adsorption. However, it will be well to postpone these estimates until the absolute value of the dielectric constant of cellulose has been definitely established. Further, the experimental apparatus in its present form is not such as to permit of the estimation of the dielectric constant of water left by desorption. It can be predicted, however, that when this investigation is continued, information of even greater interest than that from the heat of wetting measurements will be obtained (1).

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A NOTE ON THE SPECIFIC HEATS OF LIQUID DEUTERIUM OXIDE[1]

By R. S. Brown[2], W. H. Barnes[3] and O. Maass[4]

Abstract

Preliminary determinations of the specific heats of liquid deuterium oxide from 4° to 65° C. are described. The average specific heats over the temperature ranges 4° to 26° C., 26° to 45° C., and 26° to 65° C., are 1 018, 1 003 and 1 008 respectively, while the average specific heat between 4° and 65° C. is 1 01 cal. per gm. per degree.

In a previous investigation of the specific heats and latent heat of fusion of solid deuterium oxide (3) it was found that the average specific heat of liquid D_2O is higher than that of water between 3.8° and 25° C. In the present note some preliminary determinations of the specific heats of liquid deuterium oxide over the temperature range 4° to 65° C. are described.

The adiabatic calorimeter (1) previously employed (3) was modified for the present study by replacing the inner calorimeter vessel with one of smaller capacity, and by extending the supports for the radiation thermocouple junctions in order to ensure the optimum distance (about 1 mm.) between the junctions and the wall of the inner vessel.

The 12 gm. sample of 98% deuterium oxide (3) was transferred from the platinum container to a Pyrex bulb of about 14 cc. capacity by the method outlined in the previous paper (3), and was sealed therein. The same weight of distilled water was sealed in a second Pyrex bulb of the same shape and virtually the same capacity.

The total heats of the bulbs plus D_2O and H_2O, respectively, were measured from known initial temperatures to a final temperature of 26.0° C. Oil thermostats, automatically controlled to within ±0.05°C., were employed to bring the containers and contents to the initial temperatures desired.

It was found that appreciable heat losses from the bulbs occurred during their transference from the thermostat to the calorimeter. This disadvantage in the present procedure, when results of a very high degree of accuracy are desired, has already been pointed out (2). In the present determinations these heat losses were estimated in the following manner. A series of total heat measurements of the bulb containing ordinary water for different periods of transfer was made from each initial temperature. The times of transfer were determined to within 0.1 sec. The heat losses were calculated by means of the equation.

$$h_x = (C_{H_2O}\, w_{H_2O} + C_{Py}\, w_{Py})\,(t_i - t_s) - H,$$

where h_x is the heat loss during transfer for time x.

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C_{H_2O} and C_{Py} are the specific heats of water and Pyrex, respectively, for the temperature range $(t_i - t_f)$, where t_i is the initial, and t_f the final, temperature.

w_{H_2O} and w_{Py} are the weights of water and Pyrex, respectively,

H is the total heat of the Pyrex bulb and water from t_i to t_f as measured in the calorimeter.

A curve of the heat losses plotted against times of transfer was drawn for each initial temperature. The time required to transfer the bulb containing deuterium oxide was observed for each determination, and the heat loss during the transfer was obtained from the curve for the initial temperature involved. About five experiments were made on the deuterium oxide from each initial temperature.

The total heats per gram (h_{D_2O}) of liquid deuterium oxide from the initial to the final temperature were calculated by means of the equation,

$$h_{D_2O} = \frac{H + h_x - C_{Py}\, w_{Py}\, (t_i - t_f)}{w_{D_2O}}$$

where H is now the total heat of the Pyrex container and deuterium oxide from the initial temperature, t_i, to the final temperature, t_f. as measured in the calorimeter.

It should be noted that since the weights of Pyrex and the surface areas of both bulbs were virtually the same, any error in assuming the values for C_{Py} disappears in the above expression since h_x contains C_{Py}.

Since the final temperature in the calorimeter was always within about 0.5° of 26.0° C., the total heats were corrected to this latter figure in the usual way (2).

The total heats taken up or given up by one gram of liquid deuterium oxide when warmed or cooled from various initial temperatures to 26.0° C. are given in Table I.

TABLE I

TOTAL HEATS OF LIQUID D_2O

Initial temp., °C.	4.0	26.0	45.0	65.0
Total heat, cal./gm.	−22.4	0.0	19.05	39.25

The maximum difference between the total heats observed in the different experiments from each initial temperature was less than 1%, so that the probable accuracy of the values in Table I is of the order of 0.5%. From these figures the average specific heats of liquid deuterium oxide over the temperature ranges 4° to 26° C., 26° to 45° C., and 26° to 65° C., are 1.018, 1.003 and 1.008, respectively, while the average specific heat between 4° and 65° C. is 1.01 cal. per gm. per degree.

The accuracy of the results shown above does not warrant other conclusions than that the specific heat of heavy water is slightly higher than that of ordinary water, although there appears to be a trend towards decreasing values with rise in temperature, and the minimum in the specific heat curve probably is at a higher temperature than is that for ordinary water. It is also of considerable interest to note that the molecular heat of heavy water is greater than that of ordinary water by an amount almost proportional to their differences in molecular weight.

As mentioned in the previous paper (3), certain improvements in the adiabatic calorimeter are under discussion at the present time. As these will permit the determination of the thermal constants of deuterium oxide to be made to at least one part in a thousand, it has been deemed advisable to discontinue the present investigation until the new calorimeter is completed. On account of the unavoidable delay which this will entail, it was considered to be of interest in the meantime to present the data contained in this note.

Acknowledgment

Acknowledgment is again made to the anonymous donors of a grant of \$1,000.00 for calorimetric research in this laboratory which has made possible the present investigation.

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THE REACTION PRODUCTS OF INDOLS WITH DIAZOESTERS[1]

By Richard W. Jackson[2] and Richard H. Manske[3]

Abstract

In conformity with findings of previous work on indols and in contradistinction to more recent work on pyrrols, the action of diazoesters on indol leads to 3-substituted as well as a small amount of 1 : 3-disubstituted derivatives. The formation of 2-substituted derivatives could not be demonstrated. The reaction discussed is a convenient one for the synthesis of a wide diversity of indol compounds.

Those natural derivatives of indol whose constitution has been elucidated in whole or in part, have invariably been found to carry substituents in the 3-position although the 2- and possibly the 1-position may also be occupied. Synthetically too, those derivatives with the substituents in the 3-position are in general more readily available, and this is particularly true when the substituents carry reactive groups which lend themselves to further syntheses.

The direct introduction of substituents into the pyrrol or alkyl-pyrrol nucleus leads to 2-substituted derivatives when this position is available. As examples, the synthesis of pyrryl-2-acetic acid by the action of ethyl diazoacetate on pyrrol (5), and the synthesis of 2-methylpyrryl-5-succinic acid (1) by the reaction between 2-methylpyrrol and maleic anhydride, may be cited. The latter of these reactions when applied to indol yields unexpected products (2). The action of ethyl diazoacetate on 1-methylindol, however, was found by Piccinini (6) to yield 1-methylindolyl-3-acetic acid, and 2-methylindol yields the corresponding 3-acetic acid. Nevertheless it seemed desirable to reinvestigate this reaction with indol to ascertain whether indolyl-2-acetic acid was one of the reaction products. The isolation of indolyl-3-acetic acid proved to be facile enough and in some respects this synthesis is the most satisfactory yet recorded (3). The presence of indolyl-2-acetic acid could not be demonstrated.

When an excess of the diazoester was employed there was obtained a moderate yield of indylene-1 : 3-diacetic acid*. This substance is of some interest in that heating or distilling it *in vacuo* eliminates only one carboxyl group, and this observation is pertinent in connection with its constitution. In view of the ready loss of carbon dioxide from indolyl-3- and from 1-methylindolyl-2-acetic acid (3), the decarboxylated product is formulated as 3-methylindolyl-1-acetic acid. The highly purified dibasic acid gives a coloration with Ehrlich's reagent only with difficulty, and in this respect resembles 1-methyl-

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[1] *Manuscript received June 10, 1935.*
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**It is proposed to use the term indylene for the disubstituted derivatives of indol in analogy with the term phenylene.*

tryptophane (7). The decarboxylated product reacts normally to the test. No tri-substituted product could be isolated even when a large excess of the diazoester was employed, and the attempted condensation of 2 : 3-dimethylindol yielded only the unchanged starting material together with the decomposition products of the diazoester.

While it is improbable that 2-substituted indols will become available by this method, an extension of the reaction to another diazoester, namely, diethyl diazosuccinate, has indicated a route by which a great diversity of indol-3-substituted derivatives may be prepared. The reaction product in the case cited is indolyl-3-succinic acid, which on gentle heating loses one carboxyl group and yields the known β-3-indolylpropionic acid.

Incidentally, another synthesis of indolyl-3-acetic acid is recorded. While of no particular merit for obtaining the unsubstituted acid, because of mediocre yields, the method, it is felt, may offer distinct advantages in connection with some derivatives of the acid. Diethyl β-cyanopropionacetal (4) was hydrolyzed to the corresponding acid, which was then hydrolyzed by means of hydrochloric acid to the semi-aldehyde of succinic acid, and the latter without being isolated was condensed with phenylhydrazine. The product, subjected to the Fischer indol synthesis, yielded the required acid.

In conclusion it is pertinent to note that the attempted condensation of 2 : 5-dimethylfuran* yielded no acidic products other than those derived from the decomposition of the ester.

Experimental

Indolyl-3-acetic Acid and Indylene-1 : 3-diacetic Acid

A dried ethereal solution of ethyl diazoacetate prepared from 50 gm. of glycine ester hydrochloride was slowly run into a Claisen flask (fitted with a long fractionating column) in which had been placed 19 gm. of indol and a trace of copper powder. The ether was rapidly distilled off as the solution was run in, so that the reaction was thus made to proceed smoothly. Finally, the product was heated to 100° C. in the vacuum of a water pump, transferred to a Claisen flask and distilled at 2 to 3 mm. There was frequently a second evolution of gas at this stage, and this was particularly pronounced in the experiment in which the proportionate quantity of diazoester was greatly increased.

The almost colorless distillate was hydrolyzed with an excess of methanolic potassium hydroxide, the solution diluted with water and the methanol distilled off. Thorough extraction of this solution with ether yielded 2 gm. of indol. The alkaline solution was then acidified with hydrochloric acid and again exhaustively extracted with ether. The combined extracts were dried with sodium sulphate and the ether distilled off. The solid, reddish residue was transferred to a suction funnel and washed with cold ether.

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*We are indebted to Mr. A. F. G. Cadenhead of Shawinigan Chemicals Ltd. for a gift of this furan.

The indolyl-3-acetic acid readily dissolved in the ether and was recovered from the filtrate by removal of the solvent. It was recrystallized from a concentrated solution in ethyl acetate by the addition of benzene, or from hot water. The latter solvent is preferable when the acid is already of a good grade. In either case, the adequately purified product melted at 167 to 168° C.*, with the evolution of carbon dioxide, and this melting point was not lowered when the material was admixed with a specimen prepared from indolyl acetonitrile or one synthesized by the method to be detailed later.

The residue from the ether extraction was washed cautiously with cold ethyl acetate and then dissolved in the same solvent at the boiling point. The solution was treated with charcoal, filtered and evaporated to a small volume and, when cooled somewhat, treated with dry ether. This induced almost immediate crystallization. The product, filtered off, washed and dried, melted at 238° C. with evolution of carbon dioxide. Repetition of the purification raised the melting point to 242°. The diacetic acid is moderately soluble in warm water and methanol, but sparingly soluble in cold ethyl acetate or ether. The purest specimen gave no immediate color with Ehrlich's reagent. Calcd. for $C_{12}H_{11}O_4N$: N, 6.03%. Found: N, 5.93%. (Kjeldahl.) Neutralization equivalent: calcd., 116.5; found, 115. The yield of indolyl acetic acid was 12 gm. and that of the diacetic acid was 1.2 gm.

In a second experiment 35 gm. of indol and the diazoester ester from 150 gm. of glycine ester hydrochloride were employed, and the product, worked up as described above, yielded a small amount of indol, 10 gm. of indolyl-3-acetic acid and about four grams of indolyene-1 : 3-diacetic acid. The mother liquors of the acid fraction were submitted to further exhaustive fractionation. Small amounts of both the acids mentioned above were isolated but no new acid was discovered at any stage of the work.

3-Methylindolyl-1-acetic Acid

The diacetic acid described above was heated in an oil bath to 240° C. under slightly reduced pressure until the evolution of carbon dioxide ceased, and then distilled at 3-4 mm. The distillate was extracted with aqueous sodium bicarbonate and then the filtered solution was extracted several times with ether, acidified and again extracted with ether. The last extract was dried with sodium sulphate and the solvent largely removed. Cautious addition of benzene induced rapid crystallization. The acid, filtered off and washed with benzene and then recrystallized from ether-benzene, melted sharply at 178° C. It gave an intense pink color with Ehrlich's reagent. The acid is moderately soluble in hot water and crystallizes in slender needles. Calcd. for $C_{11}H_{11}O_2N$: N, 7.41%. Found: N, 7.49%. (Dumas.)

Indolyl-3-succinic Acid

A dried ether solution of diethyl diazosuccinate prepared from 112 gm. of aspartic acid ester hydrochloride was slowly added to 58 gm. of indol and a trace of copper powder in a Claisen flask equipped with a condenser for distillation. The reaction mixture was kept hot by means of the steam bath. Nitrogen was copiously evolved but the reaction never became violent. When the reaction had ceased the mixture was freed of readily volatile products by heating the reaction mixture to 100° C. under the vacuum created by a water pump. The oily residue was then distilled at 5 mm. At first indol distilled and as the temperature rose a gas was evolved. The gas evolution ceased in a short time and the main fraction distilled at about 250° C. The distillate was hydrolyzed with an excess of methanolic potassium hydroxide. A considerable quantity of water was added, the methanol boiled off and the cooled solution repeatedly extracted with ether; 35 gm. of indol was thus recovered. The alkaline solution was acidified with dilute sulphuric acid. No precipitate was obtained. The solution was extracted repeatedly with ether, the combined extracts washed once with a little water and dried over sodium sulphate, and the solvent removed. The dark oily residue rapidly crystallized, and in this condition was only moderately soluble in ether. A dark tarry impurity was removed by two successive charcoal treatments in the minimum volume of hot water. On cooling, a copious yield of almost colorless indolyl-3-succinic acid was obtained. This melted at 198° C. with evolution of carbon dioxide. The total yield of acid including that recovered from the mother liquors was 21 gm.

**All melting points are corrected.*

The bulk of the indol succinic acid was esterified with absolute ethanol and hydrogen chloride and subsequently distilled at about 200° C. at 3 mm. A specimen of the ester, twice recrystallized from benzene and petroleum ether and then once from benzene, melted at 79–80° C. The pure white crystals were apparently solvated because upon standing they lost both weight and lustre. Calcd. for $C_{16}H_{19}O_4N$: N, 4.85%. Found: N, 5.16%. (Dumas.)

The remainder of the ester was hydrolyzed with ethanolic potassium hydroxide and the indolyl succinic acid recovered. The purest material was secured from the potassium salt which separated from the cooled alcohol solution. The acid, after crystallization from hot water (charcoal), was beautifully crystalline and melted at 199° C. However during the purification, the substance assumed a slight pinkish cast. This property recalls the similar behavior of the related indolyl-3-acetic acid. The recoveries of the ester and acid were virtually quantitative. Calcd. for $C_{12}H_{11}O_4N$: N, 6.01; C, 61.8; H, 4.76%. Found: N, 5.90, and 6.19 (Dumas); C, 62.2; H, 4.70%.

One gram of the dibasic acid was cautiously heated over a free flame until the evolution of carbon dioxide ceased. The residue was recrystallized once from hot water, then dissolved in aqueous sodium carbonate, regenerated from the solution after treating with charcoal and filtering, and recrystallized from hot water. Colorless plates of β-3-indolyl-propionic acid, melting at 131° C. either alone or admixed with an authentic specimen, were thus obtained.

Indolyl-3-acetic Acid

A solution of 47 gm. of β-cyano-propionacetal (4) in 75 cc. of methanol was treated with 17 gm. of potassium hydroxide in 25 cc. of water. The mixture was slowly evaporated on a steam bath. It was then treated with 400 cc. of water in two portions and evaporated after each addition. The residue was dissolved in 400 cc. of water, and the solution clarified by filtration (charcoal). The filtrate was heated on a steam bath for an hour with 40 cc. of concentrated hydrochloric acid and then treated with an excess of sodium acetate. A clarified solution of 33 gm. of phenylhydrazine in dilute acetic acid was added. The oily phenylhydrazone, which was at once precipitated, was extracted with ether. The solvent was removed and the residue freed of moisture by heating at 100° C. with suction. The residue was then heated under reflux with a solution of 30 gm. of sulphuric acid in 140 cc. of absolute ethanol for four hours. Much water was added and the oily product extracted with ether, washed with aqueous sodium bicarbonate, and dried over sodium sulphate. The residue obtained on removal of the ether was distilled *in vacuo.* The fraction boiling at 172 to 178° C. at 2 mm. was hydrolyzed with methanolic potassium hydroxide. The solution was diluted with water, freed of methanol, and filtered after treatment with charcoal. Cautious addition of dilute hydrochloric acid to the filtrate yielded a crystalline acid which was filtered off, washed with water, dried, and washed with benzene. This product when recrystallized from hot water, or from ether-benzene, yielded flat colorless plates melting at 167° C. with the elimination of carbon dioxide and the production of 3-methylindol. Admixture with an authentic specimen of indolyl-3-acetic acid prepared from indolyl-3-acetonitrile or with a specimen prepared from indol and ethyl diazoacetate caused no depression in the melting point.

Acknowledgment

The authors are grateful to Mr. H. Laidlaw for preparing a pure specimen of 2 : 3-dimethylindol and for assistance in some of the experiments with the ethyl diazoacetate.

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RECHERCHES SUR LA MATIÈRE AROMATIQUE DES PRODUITS DE L'ÉRABLE À SUCRE[1]

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Résumé

La matière aromatique du sirop et du sucre d'érable est un produit complexe, très instable, formé d'une partie solide et d'une partie liquide résineuse. La partie solide contient de la vanilline et de l'acide vanillique. La partie résineuse fournit, après dédoublement par l'émulsine, du gaiacol. Les extraits de la sève d'érable ne contiennent pas la matière aromatique du sirop et du sucre; celle-ci se développe seulement durant la cuisson. La sève contient de la vanilline, de l'acide vanillique et du gaiacol. La concentration de ces dérivées phénoliques dans la sève est de 0 5 parties par million. Il se forme une quantité additionnelle de substances phénoliques au cours de la cuisson. La substance aromatique donne en milieu alcalin des phénolates inodores et de couleur brun foncé. Un sirop aromatique et peu coloré doit donc être préparé à un pH inférieur à 7. La coloration jaune ou brune du sirop n'est pas due essentiellement à la formation de caramel.

L'écorce de l'érable contient une glucosidase qui hydrolyse la coniférine et l'amygdaline; elle est semblable à l'émulsine, nous l'appelons "Acérase". La sève d'érable contient un ferment du type de l'amylase qui dédouble l'amidon de l'arbre en un disaccharide de nature non déterminée, et qui est actif même à des températures relativement basses.

Le bois d'érable contient très peu de coniférine, laquelle se transforme, vers le 1er septembre, en substances résineuses de nature ligneuse. Les graines d'érable ne contiennent pas de coniférine, mais la même substance aromatique que le sirop. La coniférine peut être la substance-mère de la vanilline dans le bois et la sève d'érable. Dans l'extrait aromatique du sirop il n'y a pas de coniférine, d'alcool et d'aldéhyde coniférylique et de "Sulfitlaugenlakton".

L'arome des produits de l'érable est principalement dû à la formation d'hadromal au cours de la cuisson de la sève. A côté de l'hadromal, il peut y avoir de très faibles quantités d'autres matières aromatiques. La sublimation destructive de l'hadromal donne de la vanilline, du gaiacol et de l'acide vanillique, tout comme les extraits aromatiques du sirop d'érable. La synthèse de l'hadromal peut se réaliser à partir du sucrose (furfural), de la vanilline et du gaiacol. Il est probable que l'hadromal ne se trouve pas à l'état libre dans les bois; l'hadromal de Czapek et de Combes est plutôt formée par synthèse catalytique à partir des dits fragments de la lignine.

Introduction

Les trois espèces d'érables, *Acer saccharum*, *Acer saccharinum* et *Acer rubrum* fournissent au printemps une sève sucrée qui donne par évaporation à grande surface du sirop et du sucre à arome caractéristique. Nelson (12), qui voulait identifier la nature chimique de cette substance aromatique, arrive à la conclusion: "Investigation of the flavor of maple syrup showed that it depends to a great extent on an unstable phenolic substance which is associated with a crystalline aldehyde melting at 74–76° and similar in odor and properties to vanillin. Maple syrup may contain minute quantities of other aldehydic substances which influence the flavor". Snell (16) dit que le principe aromatique est identique ou semblable à la vanilline, par suite de l'odeur et des propriétés des extraits. L'un de nous (14) a établi des méthodes de dosage des fonctions phénoliques et aldéhydiques dans les produits de l'érable, permettant de distinguer des nombreux produits falsifiés les produits authentiques de l'érable. Le but du présent travail était de préciser nos connaissances sur l'origine et la nature chimique du principe aromatique des produits de l'érable.

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Partie théorique

1. Extraction et propriétés des extraits du sirop et de la sève

Par extraction à l'éther d'un sirop dilué, traité par l'émulsine à 25–35° C. pendant 2 semaines, on obtient un résidu brun, résineux, très aromatique. Une partie du résidu est soluble dans l'éther de pétrole et abandonne une substance solide blanche, associée à un produit collant. Le solide recristallisé (très faibles quantités) démontre les réactions de la vanilline.

Par extraction à l'éther de la sève d'érable fraîche, on obtient quelques aiguilles incolores disséminées dans une huile jaune. Les cristaux ont été identifiés comme acide vanillique. La purification de la partie huileuse était impossible.

Dans la sève fraîche traitée par l'émulsine, on a pu constater, après extraction à l'éther, la présence de gaiacol, qui doit donc se former par hydrolyse d'une substance plus complexe contenue dans la partie résineuse des extraits de sirop et de sève.

La concentration en substances phénoliques (vanilline et gaiacol) de la sève est de 1/2,000,000 dosées comme vanilline. Vu que l'on concentre la sève à 1/20 de son volume dans la fabrication du sirop et que les sirops contiennent de 20 à 70 parties de phénols par million (14), on doit conclure qu'une quantité additionnelle de phénols libres se forme par hydrolyse durant la cuisson.

La partie phénolique de la substance aromatique donne, par extraction de la solution étherée à la soude, un phénolate inodore et coloré en brun. En acidulant prudemment on obtient après une autre extraction un résidu à odeur voisine de celle de la vanilline. Elle explique aussi la raison pour laquelle un bon sirop peu coloré et très aromatique doit être préparé à un pH inférieur à 7.

En soumettant, à titre de comparaison, une solution diluée de caramel à une extraction analogue, on constate que le pigment est insoluble dans l'éther et que l'agitation avec de la soude ne produit aucune coloration. Le pigment brunâtre du sirop n'est donc pas dû essentiellement à la formation de caramel pendant la cuisson, contrairement à ce que prétend Balch (1); au contraire, la coloration du sirop dépend en majeure partie de la substance aromatique elle-même colorée.

2. Les agents hydrolytiques de l'érable

Dans le but d'étudier certains dédoublements hydrolytiques, nous avons recherché des ferments dans l'arbre vivant.

L'extraction de l'écorce d'érable fournit une glucosidase du type de l'émulsine, que nous voudrions appeler "Acérase"; elle hydrolyse la coniférine et l'amygdaline.

La sève d'érable contient un autre ferment du type de l'amylase et qui dédouble rapidement l'amidon, contenu en grandes quantités, au printemps, dans les cellules des racines, des jeunes tiges et de l'assise de croissance de l'érable. La sève ne donne pas la réaction de l'amidon, mais le ferment qu'elle contient doit être une amylase de saccharification, qui est active, d'après Müller-Thurgau, déjà à des températures voisines de 0°. Il nous a cependant été impossible de trouver du maltose dans la sève, quoique la présence d'un disaccharide autre que le sucrose soit probable.

3. *La substance aromatique en rapport avec la coniférine, l'alcool et l'aldéhyde coniférylique*

La présence de vanilline dans la sève et dans les extraits de sirop d'érable, ainsi que d'une glucosidase dans l'écorce nous a conduit à rechercher l'origine de la matière aromatique dans la coniférine très répandue dans le règne végétal.

En appliquant la méthode de Tiemann et Haarmann (18) au bois d'érable, il nous a été possible d'extraire du cambium un peu de coniférine, mais avec un rendement beaucoup plus faible que dans le cas des conifères. Après le 1er septembre, l'érable n'a presque plus de sève et le cambium du jeune bois ne contient plus de coniférine; l'extraction donne seulement un résidu résineux à odeur de vanilline et démontrant les réactions de la lignine.

Par extraction des graines d'érable on obtient une substance résineuse qui ne contient pas de coniférine, mais qui est aussi aromatique que les extraits de sirop d'érable.

La présence de coniférine dans le bois d'érable établie, nous avons voulu examiner si la matière aromatique contenait son produit d'hydrolyse, l'alcool coniférylique, ou son produit d'oxydation, l'aldéhyde coniférylique, ou un dérivé de polymérisation, appelé "Sulfitlaugenlakton". Nous avons préparé ces corps à titre de comparaison; ils ont des propriétés nettement différentes de la vanilline et des extraits de sirop et ne se trouvent pas à l'état libre dans la matière aromatique de l'érable.

4. *La substance aromatique en rapport avec l'hadromal*

L'hadromal a été isolée du bois par Czapek (4), et plus tard par Combes (3) et par Hoffmeister (7). Grafe (5) prétend qu'elle est composée de vanilline, méthylfurfural et pyrocatéchine. A cause de sa composition et à cause des propriétés aromatiques fort intéressantes que ces auteurs donnent, nous avons entrepris l'étude de l'hadromal.

Dans les produits de l'érable, nous avons isolé la vanilline et l'acide vanillique, mais nous n'avons pu déceler le furfural et le méthylfurfural, quoique la cuisson du sucrose en solution faiblement acide doive entraîner la formation de ces produits. Voici la raison: En concentrant une solution de sucrose faiblement acide, on constate après peu de temps la présence de furfural (papier d'acétate d'aniline); mais si on ajoute de la vanilline, la réaction du furfural n'apparaît que beaucoup plus tard. Il semble donc que la vanilline entre immédiatement en réaction avec le furfural naissant, ce qui se produirait aussi dans la concentration de la sève d'érable dont le pH est ordinairement en bas de 7.

Nous n'avons jamais pu isoler la pyrocatéchine dans toutes nos extractions de sirop et de sève, mais nous y avons trouvé son éther monométhylique, le gaïacol. L'hadromal devrait donc contenir un reste gaïacolique et non un reste pyrocatéchique, ce qui est d'autant plus probable si on considère les propriétés de l'hadromal qui ressemblent beaucoup à celles de la lignine, et le fait que Lüde (11) a obtenu du gaïacol et de l'acide vanillique comme principaux produits de dédoublement dans la sublimation de la lignine du bambou.

En soumettant l'hadromal, préparée d'après Czapek (4), à une sublimation destructive dans l'appareil décrit par Lüde, nous avons aussi obtenu du gaïacol et de l'acide vanillique. Les conditions et les résultats sont indiqués dans le tableau No. 3. En opérant dans les mêmes conditions sur un extrait aromatique de sirop d'érable, on obtient les mêmes produits, mais avec un rendement plus faible.

Afin de prouver davantage que l'hadromal est un des principaux constituants aromatiques des produits de l'érable, nous avons essayé de faire sa synthèse. En effet, il nous a été possible de prouver de çette façon, que l'hadromal est composée de furfural, de vanilline et de gaiacol, et non de méthylfurfural, vanilline et pyrocatéchine, comme le prétend Grafe. En chauffant une solution de sucrose avec de la vanilline et du gaiacol dans des conditions déterminées, on obtient une très faible quantité d'une substance identique à l'hadromal dans ses propriétés, et ayant l'arome des extraits de sirop d'érable. En omettant le sucrose, il ne se forme pas de trace d'hadromal, ce qui prouve qu'il y a, dans le premier cas, formation intermédiaire de furfural ou de oxyméthylfurfural. En répétant l'expérience avec de l'a-oxyméthylfurfural, préparé d'après Kiermayer (10), à la place du sucrose, le résultat est encore négatif. Il faut donc admettre la formation de furfural, lequel se combine immédiatement avec la vanilline, tel que déjà mentionné.

L'hadromal se forme encore mieux en chauffant les dits ingrédients d'abord en milieu acide, ensuite en milieu alcalin de pH convenable. L'extrait ètheré du produit de réaction possède un arome très développé et identique à celui des produits de l'érable.

Nous avons enfin étudié l'action de certains catalyseurs autres que l'acétate de manganèse, en particulier l'acétate de plomb et le chlorure stanneux. Ces deux sels catalysent la synthèse de l'hadromal positivement. Cette observation est importante au point de vue théorique, si on considère que Czapek et Combes, ont isolé l'hadromal du bois en présence d'un excès de l'un ou de l'autre des deux sels. Nous sommes portés à croire que l'hadromal, aldéhyde instable, n'existe pas à l'état libre dans les bois et que ces auteurs l'ont involontairement synthétisé au cours de leurs opérations, à partir du suc cambial qui contient, à côté de sucrose, plusieurs produits de métabolisme de la lignine, tels que la vanilline et le gaïacol. Déjà Keppeler (9) avait mis l'existence de l'hadromal dans la nature en doute, et nos expériences devraient le prouver définitivement.

Cette idée est d'ailleurs appuyée par l'histoire génétique du principe aromatique des produits de l'érable. La sève ne contient pas de trace d'hadromal ou autre matière aromatique caractéristique pour le sirop et le sucre. L'arome se forme entièrement au cours de l'évaporation de la sève à grande surface et en présence d'air. Cette synthèse se fait à partir du sucrose, de la vanilline et du gaiacol présents dans la sève. Nous avons réalisé la combinaison en hadromal en dehors des évaporateurs de la cabane à sucre. La synthèse de l'arome doit être une oxydation lente, car elle ne se produit pas par concentration de la sève dans le vide ou en présence d'un gaz inerte.

L'arome caractéristique du sirop et du sucre d'érable est donc principalement dû à la formation d'hadromal au cours de l'évaporation de la sève. Vu que la finesse de l'arome varie souvent selon l'origine des produits et les soins apportés à leur fabrication, il peut y avoir, à côté de l'hadromal, des traces d'autres matières aromatiques, par exemple des glucides phénolaldéhydiques ou des résines formées par polymérisation de l'hadromal instable.

Nous continuons nos travaux dans le but d'isoler d'autres matières aromatiques, d'étudier le mécanisme exacte de la formation de l'hadromal et d'élucider sa constitution dont la connaissance avancerait sans doute la chimie de la lignine

Partie expérimentale

1. EXTRACTION ET PROPRIÉTÉS DES EXTRAITS DU SIROP ET DE LA SÈVE

a. Extraction du sirop

A 18 litres de sirop d'érable à 30% de sucre, nous avons ajouté de l'émulsine extraite d'amandes amères (2), et comme préservatif, une solution de fluorure de sodium formant 1% dans le mélange. Le tout est demeuré pendant 14 jours à une température variant entre 25–35°. Nous avons ensuite extrait ce sirop deux fois avec 200 et 100 cc. d'éther par litre; l'excès du solvant distillé dans le vide, nous avons obtenu un résidu amorphe, brun et résineux, d'arome d'érable très prononcé. En traitant cette substance par l'éther de pétrole, une partie se dissout, et le résidu, repris par l'acétate d'éthyle, ne démontre aucune tendance à la cristallisation. La partie soluble dans l'éther de pétrole dépose des aiguilles groupées en rosettes, très aromatiques Après une autre cristallisation de l'éther de pétrole, il se forme un peu de résine, qui, absorbée par une plaque poreuse, laisse une substance solide blanche en très faible quantité. Recristallisée de l'éther de pétrole, elle se présente en aiguilles incolores groupées en rosettes et semble être très pure et uniforme. Très instable, elle devient collante après quelques heures seulement passées dans un desiccateur à vide; elle se ramollit alors vers 60° et donne, sans passer par un point de fusion déterminé, une résine jaune qui ne se solidifie plus après refroidissement.

Cet extrait donne les réactions de coloration suivantes:— acide sulfurique concentré–jaune, puis brun chocolat; chlorure de fer–bleu verdâtre; aniline–jaune pâle; phloroglucine et acide chlorhydrique–rose clair; benzidine et acide acétique–jaune pâle.

L'extrait contient sans doute de la vanilline, laquelle donne les mêmes réactions, excepté avec l'acide sulfurique, qui provoque une coloration jaune seulement, mais tous deux précipitent des flocons blancs par addition d'eau. Cette différence est probablement due à la présence d'une autre substance que nous étudierons plus loin.

b. Extraction de la sève d'érable

Dix-neuf litres de sève fraîche ont été extraits à l'éther, et celui-ci, desséché sur du chlorure de calcium, a été distillé dans le vide. Le résidu a formé une huile jaune, contenant plusieurs cristaux en forme d'aiguilles. Par un lavage rapide à l'éther de pétrole et par une recristallisation de l'éther ordinaire, il s'est déposé une substance blanche, cristallisée en aiguilles groupées en étoile, que nous avons identifiée comme étant de l'acide vanillique: P.F. 207°; P.F. mixte, 207° C.

Il y a toujours à côté de cette substance cristalline une forte proportion d'une huile résineuse jaune, d'odeur forte de vanilline, mais il nous a été impossible de la purifier pour isoler cette dernière.

c. Présence du gaïacol dans la sève

On abandonne 9 litres de sève pendant deux semaines avec de l'émulsine et on extrait à l'éther. Dans le résidu huileux, on peut déceler le gaïacol par l'odeur et les réactions de coloration.

d. Dosage des corps à fonction phénolique dans la sève

Nous avons employé la méthode de Folin et Denis (19). Comme solution témoin, on s'est servi d'une solution de vanilline 1/500,000; 5 cc. de la solution témoin ont donné la même coloration que 20 cc. de sève d'érable. La concentration en substances phénoliques de la sève d'érable est donc de 1/2,000,000, calculée comme vanilline.

e. Formation de phénolates

Nous avons extrait un gallon de sirop authentique avec de l'éther, et agité la solution éthérée avec une solution aqueuse de 5% de soude. La dernière s'est colorée en brun, tandis que la solution éthérée s'est décolorée et cela après une seule extraction à la soude. La partie aqueuse neutralisée avec prudence par une solution de 5% d'acide chlorhydrique tourne au jaune clair au point de neutralité. Extrait de nouveau à l'éther, le résidu, après évaporation du solvant, possède une odeur très voisine de la vanilline, sans être absolument identique.

2. LES AGENTS HYDROLYTIQUES DE L'ÉRABLE

a. Extraction de l'"Acérase" de l'écorce d'après la méthode de Bertrand et Thomas (2)

Les écorces d'érable broyées en poudre ont été traitées par l'eau pendant trois jours en présence de fluorure de sodium, comme préservatif. La solution filtrée a été traitée par deux fois son volume d'alcool à 95%, et une substance blanche floconneuse s'est précipitée, qui, redissoute dans l'eau, a été essayée sur une solution de coniférine de la façon suivante:

I. Solution de 1% de coniférine plus 1% de fluorure de sodium.
II. Solution de ferments extraits des écorces plus 1% de fluorure de sodium.
III. Solution de 1% de coniférine plus ferments extraits des écorces plus 1% de fluorure de sodium.

Ces trois solutions ont été placées dans l'étuve maintenue à 37° C. pendant sept jours. Après ce temps, le glucose formé a été dosé de la façon ordinaire par la liqueur de Fehling, le précipité d'oxyde cuivreux a été redissout dans le mélange d'acide sulfurique et de sulfate ferrique, et le sulfate ferreux formé a été dosé par une solution de permanganate de potassium *N*/100. Les résultats sont indiqués dans le tableau No. 1.

TABLEAU No. I.

		$KMnO_4$ (N/100), cc.
I	20 cc. de sol. Fehling (3 min. d'ébullition)	0 4
II	20 cc. de solution de ferment plus 20 cc. de sol. Fehling	0 4
III	20 cc. de sol. de coniférine plus 20 cc. de sol. Fehling	0 4
IV	20 cc. de sol. de coniférine plus 2 cc. de sol. de ferment plus 20 cc. de sol. Fehling.	1 2

La quantité indiquée de permanganate employé correspond à la quantité de glucose formée.

La consommation de quantités constantes de permanganate dans les trois premiers cas, considérés comme essais à blanc, est due exclusivement à l'autoréduction de la liqueur de Fehling à la température d'ébullition. Dans le quatrième cas, on constate nettement que la coniférine a été hydrolysée par l'extrait des écorces, la quantité de glucose formé étant même appréciable.

b. Extraction de l'"Acérase" de l'écorce d'après la méthode de Schneegans (15)

Les écorces pulvérisées ont été traitées par quatre fois leur poids de glycérine, et abandonnées pendant trois semaines à la température du laboratoire. La glycérine a ensuite été filtrée, centrifugée, et les ferments ont été précipités par l'alcool et redissouts dans l'eau. Les essais d'hydrolyse effectués avec cet extrait sur de l'amygdaline ont été exécutés comme ceux que nous avons faits sur la coniférine.

TABLEAU No. 2

		$KMnO_4$ (*N*/100), cc.
I	20 cc. de sol. Fehling (3 min. d'ébullition)	0.4
II	15 cc. de sol. de ferments plus 20 cc. de sol. Fehling	0 4
III	15 cc. de sol. d'amygdaline plus 20 cc. de sol. Fehling	0.8
IV	15 cc. de sol. d'amygdaline plus 2 cc. de sol. de ferments plus 20 cc. de sol. Fehling.	1.9

On remarque que l'amygdaline en solution aqueuse est déjà un peu dédoublée par la chaleur. L'écart entre III et IV est assez grand cependant pour constater sans aucun doute que, dans le quatrième cas, un ferment est entré en action.

c. Preuve pour la présence dans la sève d'un ferment du type de l'amylase

Nous avons préparé une suspension aqueuse de 0.5% d'amidon, additionnée de 1% de fluorure de sodium, et avons laissé couler la sève d'érable dans cette solution contenue dans un récipient stérilisé, attaché au "chalumeau". Après trois heures, nous avons obtenu la réaction des dextrines, et après six heures, tout l'amidon a été transformé en disaccharide. Nous avons réussi à faire dédoubler de cette façon jusqu'à 20 cc. d'une suspension de 1% d'amidon, durant une journée. Ce ferment travaille encore vite à des températures relativement basses, de 0 à 15° C., température de la coulée printanière.

3. LA SUBSTANCE AROMATIQUE EN RAPPORT AVEC LA CONIFÉRINE, L'ALCOOL ET L'ALDÉHYDE CONIFÉRYLIQUE

a. Extraction de la coniférine du bois d'érable

Au cours de l'été, nous avons appliqué la méthode de Tiemann et Haarmann (18), en grattant le cambium d'érable avec des morceaux de verre, mais la solution filtrée et concentrée n'a pas déposé de cristaux de coniférine après concentration au cinquième. Nous avons poussé la concentration plus loin; il s'est formé une solution résineuse qui empêchait toute cristallisation, mais qui donnait les réactions de la coniférine.

Nous avons cependant réussi à démontrer sa présence plus nettement par extraction d'une petite quantité de cambium frais d'érable, par l'alcool amylique; après la distillation de l'excès du solvant, nous avons obtenu une faible quantité de dépôt, cristallisé en feuillets, semblables à ceux que l'on obtient par cristallisation de la coniférine du cyclohexanone. Ce produit donne une coloration violette avec de l'acide sulfurique concentré, et toutes les autres réactions de la coniférine. Après une nouvelle recristallisation de l'eau chaude, on obtient des feuillets uniformes qui dégagent, après quelque temps, l'odeur de la vanilline.

Après le 1er septembre, nous avons enlevé des copeaux de jeune bois d'érable (cambium), et les avons fait bouillir avec de l'eau. Cet extrait aqueux a été repris par l'éther, qui a entraîné des résines à forte odeur de vanilline, ensuite extrait par l'alcool amylique. Le résidu, après évaporation du solvant, possède l'odeur caractéristique de la vanilline et ne donne pas les réactions de la coniférine, mais bien des réactions semblables à la lignine.

b. Extraction des graines d'érable

Nous avons pris 40 g. de graines, dont l'écorce avait été enlevée, et nous les avons extraits par l'alcool dans un Soxhlet, pendant six heures. La solution alcoolique se colore fortement en jaune verdâtre, et le résidu laissé après distillation de l'alcool est résineux et brun. Cette résine dissoute dans l'eau et de nouveau extraite par l'éther a donné un résidu toujours résineux, et aussi aromatique que les extraits provenant du sirop d'érable. Toutes les tentatives de faire cristalliser cette résine ont échoué, et nous n'avons pu déceler la coniférine dans cet extrait de graines d'érable.

c. *Préparations comparatives*

L'alcool coniférylique a été préparé par hydrolyse de la coniférine d'après F. Tiemann (17), l'aldéhyde coniférylique par la méthode de Pauly et Feuerstein (13) modifiée par Hillmer et Hellriegel (6), et la "Sulfitlaugenlakton" d'après B. Holmberg (8).

4. LA SUBSTANCE AROMATIQUE EN RAPPORT AVEC L'HADROMAL

a. *Préparation de l'hadromal*

Nous avons "isolé" l'hadromal du bois de chêne en suivant les méthodes de Czapek (4), de Combes (3) et de Hoffmeister (7). Dans tous les cas nous n'avons obtenu que des traces d'hadromal.

b. *Sublimation destructive de l'hadromal*

Nous avons soumis l'hadromal obtenu selon la méthode de Czapek à une sublimation dans l'appareil imaginé par Lüde (11); le tableau No. 3 résume les résultats:

TABLEAU No. 3

Temps, min.	Température, °C.	Produits obtenus
10	40	Gouttelettes d'eau, odeur de vanilline
20	60	
30	80	
40	100	
50	120	Substance huileuse jaune, odeur de gaïacol
60	130	
70	140	
80	150	
90	160	Aiguilles blanches dispersées dans la partie huileuse (acide vanillique).
100	170	
110	180	
120	190	

Par sublimation d'un extrait aromatique de sirop d'érable dans les mêmes conditions on obtient les mêmes produits, mais avec un rendement plus faible.

c. *Synthèse de l'hadromal*

A une solution contenant 5% de sucrose, on ajoute une quantité égale de vanilline et de gaïacol, un peu de malate de calcium, et de l'acétate de manganèse, afin d'être à peu près dans les conditions de milieu de la sève d'érable; on chauffe pendant une heure en solution faiblement acide, on rend le mélange alcalin par du carbonate de sodium, et on maintient l'ébullition pendant quatre ou cinq heures. La solution devient brune, mais elle se décolore beaucoup en la neutralisant par l'acide chlorhydrique; on extrait ensuite par l'éther. Le résidu d'évaporation de l'éther est une poudre amorphe jaune (trace), qui ne possède plus l'odeur de la vanilline et du gaïacol, mais bien une odeur caractéristique, ressemblant beaucoup à l'odeur des extraits faits sur les produits de l'érable. Cette substance fond vers 73° C.; elle donne les réactions des aldéhydes et des phénols ainsi qu'une coloration rose avec la phloroglucine, et bleu verdâtre avec le chlorure ferrique. Elle se conserve assez bien à l'air, son arome s'y développe de plus en plus; un sirop préparé avec cet extrait synthétique est identique au sirop d'érable authentique par l'arome et la saveur.

En chauffant les mêmes ingrédients d'abord en milieu acide, puis en milieu alcalin, en présence de catalyseurs, tels que l'acétate de manganèse ou le chlorure stanneux, le rendement en hadromal est meilleur, quoique l'on n'obtienne que des traces.

Remerciements

Nous adressons à M. l'abbé Alexandre Vachon, directeur de l'Ecole Supérieure de Chimie, Université Laval, nos remerciements les plus sincères pour l'encouragement précieux qu'il a bien voulu nous témoigner au cours de l'éxécution de ce travail.

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THE ACTION OF THE TWO AMYLASES OF BARLEY[1]

BY CHARLES S. HANES[2]

Abstract

Experiments described in this paper confirm the view that β-malt amylase selectively hydrolyzes one portion of the starch substance; this fraction (approximately 60% of the starch substance) is transformed into maltose and there remains a residual non-reducing fraction (erythrogranulose) which retains the property of iodine coloration. With regard to α-malt amylase, several lines of evidence indicate that this enzyme does not exert a selective action upon the erythrogranulose fraction, as is suggested in a current theory of starch constitution, but that it induces the breakdown of both fractions. In this case the reducing products do not consist exclusively of maltose.

Recent investigations indicate that the dextrinogenic component of malt amylase is an α-amylase in the Kuhn (4) sense, whereas the saccharogenic component is a β-amylase (7, 10, 14). The dextrinogenic and saccharogenic components have thus come to be designated α- and β-malt amylase, respectively.

According to Kuhn's theory the production of α-maltose by α-amylases and β-maltose by β-amylases (which in accordance with the mutarotation phenomena is assumed to occur) results from the specific hydrolysis of α- and β-glycosidic linkages in the starch molecule by the respective types of amylase. The two forms of maltose are considered to arise from the breakdown of a single substrate through alternative types of hydrolysis.

More recently van Klinkenberg (10–13) has advanced the view that the liberation of α- and β-maltose by α- and β-malt amylase is due, not to alternative types of hydrolysis of a single substrate, but to the selective hydrolysis of two components of starch which he designates α-starch and β-starch. van Klinkenberg summarizes his conception of the relations between the two starch constituents and the two malt amylases in the following schema (13, p. 91):

$$\begin{tikzcd}
\alpha\text{-starch } (36\%) \arrow[r, shift left] \arrow[d, "\text{(by } \alpha\text{-amylase)}"] & \beta\text{-starch } (64\%) \arrow[l, shift left] \arrow[d, "\text{(by } \beta\text{-amylase)}"] \\
\alpha\text{-maltose } (36\%) \arrow[r, shift left] & \beta\text{-maltose } (64\%) \arrow[l, shift left]
\end{tikzcd}$$

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[1] *Manuscript received April 30, 1935.*
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The evidence on which van Klinkenberg's hypothesis is based consists essentially of the following points:

1. When β-malt amylase has acted to completion on soluble starch the reducing power of the products corresponds to 64% of the theoretical maltose. The iodine color remains blue or blue-violet owing to the presence of a non-reducing residual material, Wijsman's erythrogranulose (15) or van Klinkenberg's α-starch, which is easily separated by alcohol precipitation. This is interpreted as a selective and complete hydrolysis of β-starch to maltose by β-amylase, the α-starch fraction remaining unattacked.

2. When α-amylase acts on starch the reducing power rises rapidly to a value that corresponds to 36% of the theoretical maltose, after which it continues to rise slowly. The initial rapid rise is interpreted as being due to the selective hydrolysis of α-starch (36% of the total substrate) to maltose. To account for the slow subsequent rise in reducing power it is postulated that the residual β-starch slowly undergoes transformation into α-starch which is hydrolyzed as it is formed. The sharp "saccharification limit" observed in digests with β-amylase is taken to mean that the converse transformation (α-starch → β-starch) does not occur under the experimental conditions.

van Klinkenberg's conception of the selective action of β-malt amylase is in general agreement with views of earlier authors. Saccharification limits varying from 60 to 67% have been reported for this enzyme, and there is considerable evidence that the reducing power is almost exclusively due to maltose. Moreover, the residual non-reducing fraction (erythrogranulose) has been described (under various names) by several authors.

With regard to the action of α-malt amylase, van Klinkenberg postulates a selectivity for the erythrogranulose fraction. Inasmuch as this view is based on the assumption that maltose is the sole reducing product, it would appear to be open to doubt since numerous observations by earlier workers suggest that various products of low reducing power are formed during the breakdown of starch by heated malt amylase (therefore, more or less pure α-amylase).

The question has accordingly been re-examined.

Methods

Macro-Copper Method for Determining Reducing Power

In general, the progress of hydrolysis has been followed by a modified Shaffer and Hartman "Combined Reagent". In the modified form the method is best adapted to a range of reducing power equivalent to 12–80 mg. of maltose.

A specimen of maltose prepared in the laboratory by the action of β-malt amylase on soluble starch was used in standardizing the method. This product was recrystallized four times according to the T. S. Harding (1) procedure. After the second recrystallization the reducing power and specific rotation remained unchanged ($[\alpha]^{20}_{D}$ in 2.5% solution, calculated for the monohydrate, was 131.4°, the moisture content being determined by drying in a high vacuum at 110° C. in the presence of cold phosphorus pentoxide).

The Yeast Removal Method

Through the kindness of the late Prof. V. J. Harding and of Dr. T. F. Nicholson in allowing the writer to make use of the facilities of their laboratories*, it was possible to apply the methods described by these authors (3) to the analysis of the reducing products formed by the two amylases. This system of sugar analysis depends upon the selective removal power under standard conditions of particular strains of yeast in pure culture, a large amount of the organism, previously washed free from reducing substances, being used for the removal.

In the present investigation two yeasts, *Monilia krusei* and *Monilia tropicalis*, have been used. From the experience of Harding and Nicholson (3) in the use of these two organisms, it would be expected that of the sugars which might be formed during starch hydrolysis, only glucose would be removed by *M. krusei*, whereas glucose and maltose would be removed by *M. tropicalis*. There remains a possibility that other sugars removable by one or other of these yeasts may be present amongst the products of starch hydrolysis. While for this reason it is not possible to state categorically that *M. krusei* removes only glucose, and *M. tropicalis*, only glucose and maltose, the converse statement can be made with assurance, namely, that reducing material which is not removed by *M. krusei* is not glucose, and that which is not removed by *M. tropicalis* is neither glucose nor maltose.

In the yeast removal method the conditions defined by Harding and Nicholson were used. The solution to be examined was diluted so that its reducing power was less than equivalent to 20 mg. of maltose per 100 ml., sufficient $N/100$ sodium hydroxide being added to bring the pH to 6.6. Portions (10 ml.) of this solution were placed in centrifuge tubes containing 0.5 gm. of washed yeast from which excess water had been removed by draining and adsorption with filter paper. The preparations were incubated for 30 min. at 40° C., the yeast being kept in suspension by occasional stirring, after which the yeast was removed by twice centrifuging for 10 min. at 3000 r.p.m., a clean tube being used for the second operation. Finally, the reducing power of untreated and yeast-treated portions of the solution were determined on 2-ml. samples by the Harding and Downs (2) Micro-Copper method. These determinations were carried out in duplicate, except when, as rarely occurred, the first two titrations differed by more than 0.03 ml. of $N/200$ thiosulphate, in which case a third determination was made.

For each experiment, yeast blank determinations were made, 10 ml. of water being incubated in the standard way with 0.5 gm. of yeast. Corrections were then made for these values which in all cases were very small, usually 0.01–0.03 ml. of thiosulphate per 2 ml. sample.†

**In the Department of Pathological Chemistry of the University of Toronto.*

†For the 20 min. heating period used in the Micro-Copper method, 1 ml. of $N/200$ thiosulphate is equivalent to 0 263 mg. of maltose or 0.112 mg. of glucose.

Preparation of the Two Amylases

The enzymes were prepared from a high grade malting barley; with minor modifications, the methods described by van Klinkenberg (10–13) have been used.

β-Malt Amylase

Ungerminated barley was ground in a special mill to remove seed coats, aleurone layer and most of the germ tissue. The product, consisting almost entirely of the starchy endosperm tissue, was ground to a fine flour in a coffee mill. A portion (500 gm.) of the flour was extracted twice with 50% alcohol at 5° C. (1400 ml. for 1.5 hr.; 800 ml. for 1.25 hr.). The combined extracts were centrifuged, and the clear solution precipitated by increasing the alcohol concentration to 80%. The precipitate was resuspended in 50% alcohol and centrifuged, and the supernatant liquor again precipitated with 80% alcohol. The precipitate was washed rapidly with 95% and then absolute alcohol, and was dried *in vacuo* first over calcium chloride and then phosphorus pentoxide. The yield was 2.4 gm. (0.57% of the dry weight of the barley flour).

α-Malt Amylase

This amylase was derived from a malt produced in the laboratory as follows: 500 gm. of barley after 24 hr. soaking in aerated water was allowed to germinate at 20–22° C. for three days, by which time the shoots were about one and one-quarter times the length of the grains. The seedlings were washed in distilled water, dried rapidly in an air current at 32° C., and ground to a flour.

The flour was extracted twice with dilute aqueous potassium dihydrogen phosphate solution (0.05%) at 5° C. (1350 ml. for 2¼ hr.; 1000 ml. for 0.5 hr.). The extracts were combined and centrifuged and alcohol was added to the supernatant liquor to give a final concentration of 60%. The precipitate was suspended in 750 ml. of water and heated to 70° C. for 15 min. to inactivate β-amylase. (It was heated from 10° to 70° in 9 min., held at 70° for 15 min., then cooled to 16° C. in 11 min.) The suspension was then centrifuged and filtered through hardened paper, and alcohol was added to give a concentration of 65%. The resulting precipitate was rapidly washed in 85%, 95% and finally absolute alcohol, and was dried *in vacuo* first over calcium chloride and then phosphorus pentoxide. The yield was 1.7 gm. (0.40% of the original dry weight of barley).

The preparations so obtained were faintly gray powders. The α-amylase is readily taken up in water to give an opalescent solution; the β-amylase dissolves with difficulty, and even after numerous changes of water an undissolved fraction remains.*

The purity of the α- and β-malt amylase preparations was tested by the Wijsman diffusion method as described by van Klinkenberg (10). Drops of dilute solutions of the enzymes are placed on plates of 20% gelatin containing

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**A routine procedure was adopted in preparing solutions of the β-amylase; the weighed amount of the preparations was triturated for one hour with several changes of water, the combined extracts then being made up to volume. Concentrations will be given in terms of original dry preparation.*

0.25% of soluble starch. Diffusion is allowed to proceed for four days at 3° C. in a vessel containing chloroform vapor. The plates are then stained with dilute iodine in potassium iodide solution.

Plates of β-amylase showed wide circular diffusion fields which were stained a rose color; those with α-amylase showed smaller colorless diffusion fields. Mixtures of the two preparations, and also unheated malt extracts gave well defined pictures of the two-enzyme type—a colorless centrum surrounded by a rose stained ring, the diameters depending on the relative concentrations of the two enzymes.

The diffusion experiments thus gave results that would be expected with pure preparations of α- and β-malt amylase.

Substrates

The following preparations have been used as substrates for the digests that will be considered. Concentrations will be specified in terms of dry weight as determined by drying at 110° C. until no further loss occurred.

Starch No. 1.—This was a commercial sample of soluble starch (Pfanstiehl Chemical Company). It had been prepared from potato starch by the method of Small (9) which consists in treatment with hot dilute alcoholic hydrochloric acid. As stored, the sample contained 10.87% of moisture and 0.21% of ash. Its reducing power (which was the lowest of several samples of this product) was 1.5% of the R.P. (reducing power) of maltose. It resembled commercial samples of Lintner soluble starch except that its solution was considerably less opalescent.

Starch No. 2.—This sample was prepared from potato starch by van Klinkenberg's modified Lintner procedure (10), which consists in leaching the raw starch for 12 days with 7.5% hydrochloric acid, the acid being renewed every two days. Its solution was only faintly opalescent; the reducing power, however, was considerably greater than that of any commercial preparations of soluble starch, and amounted to about 4% R.P. of maltose.

Starch No. 3.—This sample was prepared from maize starch by the method used for starch No. 2. Again its solution was relatively clear but the R.P. high—about 4% of the R.P. of maltose.

Erythrogranulose.—This was prepared by allowing β-amylase to act to completion on starch No. 1 and precipitating the digest with alcohol (52–70% concentration in different batches). After the precipitate had been washed in 60% alcohol, it was redissolved in boiling water and reprecipitated with alcohol. In one case the product was subjected to a second digestion with β-amylase to ensure complete removal of material hydrolyzable by this enzyme. The different preparations were uniform in that they were white impalpable powders, almost completely devoid of reducing power (less than 0.05% R.P. of maltose). In boiling water the material gives a strongly opalescent solution. Depending on its concentration it gives a blue or violet coloration with iodine.

Conditions of Hydrolysis

All digests were carried out in stoppered flasks supported in a large water bath at 35.0° C. They were kept sterile by the addition of a few drops of toluol. Digests by β-amylase were adjusted to pH 4.8, those by α-amylase to pH 5.4, by the addition of suitable acetic acid-sodium acetate mixtures, the final concentration of acetate being 0.016 *N* throughout. The pH values were determined on digest samples with the quinhydrone electrode. The selected values of pH (4.8 and 5.4) lie close to the optimal values for β- and α-amylase, respectively, as determined by Ohlsson (7) and van Klinkenberg (10).

Experimental

SECTION I. THE ACTION OF β-MALT AMYLASE ON STARCH

1. Saccharification Limit

The progress of reducing power (R.P.) was followed in a series of digests of starch No. 1 with different concentrations of β-amylase.

Digests 1 to 4

Total volume—200 ml.; pH, 4.8; starch No. 1—1.001% throughout; enzyme—5, 10, 25 and 50 mg. β-amylase in Digests 1, 2, 3 and 4, respectively. Analyses were carried out on 10-ml. samples. The R.P. values have been expressed as percentages of the theoretical maltose for complete conversion (105.6 mg. per 10 ml.). The results are shown in Table I.

TABLE I

ACTION OF β-AMYLASE ON STARCH NO. 1

Digest Mg. β-amylase/200 ml.	1 5	2 10	3 25	4 50
Time, hr.	R.P. as percentage theoretical maltose*			
1	39.2	52.6	57.5	57.6
2	53.5	57.2	58.8	58.8
5	58.4	58.9	59.8	60.0
9	59.4	59.7	59.9	59.9
22	60.2	60.9	60.8	60.8
46	60.4	60.8	60.8	60.9

**These values have been corrected for the small R.P. of the enzyme, determined separately, which correspond to 0.1, 0.2, 0.4 and 0.8 mg. of maltose per 10 ml. in the respective digests. No correction has been made for the initial R.P. of the starch which corresponds to about 1.5 mg. of maltose per 10 ml.*

These data show the existence of a sharp saccharification limit, the final value being apparently independent of the concentration of enzyme over the range investigated. (The reaction in Digest 1 may not have been completed at the end of 46 hr., but the value at this time is only 0.6% lower than that of the other digests.) This experiment would indicate that about 61% of starch No. 1 was hydrolyzed by β-amylase.

Since this value is significantly lower than the "limit" of 64% reported by van Klinkenberg (10), experiments were carried out using starches solubilized by van Klinkenberg's method (starch No. 2 and starch No. 3). For comparison, observations were also made on the hydrolysis of starch paste (prepared by heating a suspension of raw potato starch at 100° C. for one hour). The course of the reaction was followed in duplicate digests.

Digests 5 to 10

Total volume—200 ml.; pH, 4.8; enzyme—10 mg. of β-amylase throughout. Digests 5 and 6—1.003% starch No. 2 (potato); Digests 7 and 8—1.002% starch No. 3 (maize); Digests 9 and 10—0.956% starch paste (potato).

The results are given in Table II, the R.P. values, as before, being expressed as percentage theoretical maltose, the values being corrected for the small R.P. of the enzyme, but not for that of the different substrates.

TABLE II

ACTION OF β-AMYLASE ON DIFFERENT STARCH PREPARATIONS

Digest	5	6	7	8	9	10
Substrate	Starch No. 2		Starch No. 3		Starch paste	
Time, hr.	R.P. as percentage theoretical maltose					
1	—	52 0	—	50 0	—	34 2
2	60 2	60 6	61 3	59 3	40 3	39 1
5	—	62 6	—	60 8	—	43 7
9	—	63 3	—	61 6	—	46 7
24	63 3	63 6	62 5	62 8	50 9	50 5
48	63 4	63 6	62 8	62 9	53 7	53 5
73	63 4	—	62 8	—	54 7	54 8
92	—	—	—	—	55 4	55 6

The observed saccharification limits for starch No. 2 (63.4 and 63.6%) agree well with the values reported by van Klinkenberg for soluble potato starch prepared by the same method, his values varying from 63.5 to 64.7%. The observed values for solubilized maize starch (Digests 7 and 8) are 62.8 and 62.9%, which fall within the range of his values for preparations from wheat, buckwheat and arrow root starches (62 5–66.3%). The experiment, while confirming van Klinkenberg's observations on soluble potato starch prepared by his method, shows that the saccharification limit depends upon the method of solubilization.

There can be little doubt that the difference in the observed saccharification limits for the two soluble potato starch preparations is related to the considerable difference in their initial reducing power.* Thus the limits for starch No. 1 and starch No. 2 were 60.9% and 63.5%, respectively, and the initial reducing powers, 1.5% and 4.2% of the R.P. of maltose. Without information concerning the nature of the reducing substances accompanying the substrate and their fate during the digest, it is impossible to make a correction for their presence in estimating the extent of hydrolysis effected by the enzyme. For this reason, therefore, the saccharification limit found for starch No. 2 (63.5%) must be regarded as being a less reliable estimate of the extent of the selective hydrolysis by β-amylase than the value found

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**Another factor that may enter is the amount of leaching that occurs during the solubilization process and the nature of the leached material.*

for starch No. 1 (60.9%). The latter value is probably slightly too high since, as will be seen later, about one-half of the initial R.P. of starch No. 1 is due to the presence of glucose, and moreover it is probable that a trace of glucose is formed during hydrolysis. The actual increases in R.P. due to the action of the enzyme with starches Nos. 1 and 2 were respectively 59.4 and 59.3% of the theoretical maltose.

The use of starch paste, which would be desirable from many points of view, is attended by several disadvantages. Its hydrolysis is much slower as is shown by the data in Table II. This necessitates either extremely prolonged reactions (with the attendant danger of glucose formation), or the addition of extremely large amounts of enzyme preparation. Moreover, its viscous nature makes quantitative manipulation difficult.

2. *Examination of Products of β-Amylase by the Yeast Methods*

Digest 11

Total volume—200 ml., buffered at pH 4.8 (0.015 *M* acetate); enzyme—5 mg. β-amylase; substrate—0.500% of starch No. 1.

After 18.6 hr. the R.P. determined on 20 ml. by the Macro-Copper method was equivalent to 63.5 mg. (60.3% theoretical).

Samples (5 ml.) taken at 14 and 18.6 hr. were heated for five minutes in boiling water, and diluted to 100 ml., after bringing to pH 6.6 with *N*/100 sodium hydroxide. These diluted solutions were examined by the yeast methods.

In addition to the two digest samples, a soluble starch solution was also examined, and the R.P. values have been calculated for a concentration corresponding to that of the diluted digest samples (*i.e.*, 0.025%). The results are given in Table III, R.P. values being expressed in ml. of *N*/200 thiosulphate per 2 ml. diluted digest (≡0.025% starch).

TABLE III

EXAMINATION OF THE PRODUCTS BY THE YEAST METHOD

—	Total R.P.	After *M. krusei*	After *M. tropicalis*	Removal by *M. krusei*	Removal by *M. tropicalis*
Sol. starch solution	0.045	0.02	0.01	0.025	0.03
Digest sample. 14 hr.	1.17	1.13	0.02	0.04	1.15
Digest sample. 18.6 hr.	1.24	1.18	0.01	0.06	1.23

The final total R.P. by the Micro-Copper method (1.24 ml. of *N*/200 thiosulphate) corresponds to 0.32 mg. of maltose or 64 mg. per 20 ml. of undiluted digest. This is in good agreement with the value obtained by the Macro-Copper method (63.5 mg. per 20 ml.).

It will be seen that in each case *M. krusei* removes a small amount of reducing material. The amount removed increases during the hydrolysis although the increased amount removed by this yeast (0.035 ml. at 18.6 hr.) is so small as to be hardly significant. It suggests, however, that a trace of glucose is formed during hydrolysis.

The residual R.P. after treatment with *M. tropicalis* does not rise during hydrolysis, the reducing materials produced by the action of the enzyme being removed quantitatively by this organism. The results of the yeast examination are thus in accord with the accepted view that the reducing power of digests of starch by β-amylase is due almost exclusively to maltose. This was also confirmed by examinations of numerous digests by the osazone method; typical maltosazone was found exclusively in all cases, the osazone being identified by its crystalline form and its melting point after recrystallization. Moreover, in the preparation of maltose from such digests it has been observed that the properties of the first crop of crystalline sugar (which is obtained in large yield) do not differ appreciably from those of the product obtained after being recrystallized four times.

In order to determine whether reducing substances that are not removed by *M. tropicalis* (*i.e.*, reducing substances other than maltose or glucose) are produced as intermediary degradation products, the early stages of a digest of starch No. 1 by β-amylase was examined by the yeast methods. Samples were taken 3, 10, 30, 60 and 120 min. after zero time, and in addition a control digest with killed enzyme was analyzed. The results showed that from the beginning the reducing material produced by the action of the enzyme is quantitatively removed by *M. tropicalis*.

The Yield of Erythrogranulose

In the preparation of one batch of erythrogranulose an attempt was made to determine the yield.

Digest 12

Total volume—2500 ml.; pH, 4.8; substrate—5.96% starch No. 1; enzyme—100 mg. β-amylase.

After 5½ days at 35° C. the R.P. determined on 2-ml. samples was 60.5% of the theoretical maltose. At this time the enzyme was destroyed by heating the digest rapidly to boiling. On cooling, the erythrogranulose was precipitated by adding three litres of 98% alcohol (final concentration 52%). The precipitate was allowed to stand overnight, the supernatant liquor drawn off, and the precipitate filtered on a Büchner (hardened paper). The resultant cake was broken up in one litre of 70% alcohol and allowed to stand overnight, after which it was again collected on the filter, and washed with one litre of 70% alcohol (in several portions), one litre of 80%, one litre of 95% and one litre of absolute alcohol. (The vessels were washed with boiling water and the solution so obtained was precipitated with 60% alcohol. This gave a further small amount of erythrogranulose, which was combined with the main fraction prior to washing.) The material was transferred to a weighed dish and dried, first at 80° C. for 18 hr., and then for four days *in vacuo* over phosphorus pentoxide. The moisture content was then determined. The yield of dry material was 56.6 gm.

The digest contained 149.0 gm. of dry starch. The yield of erythrogranulose (56.6 gm.) thus corresponds to 38.0% of the original substrate. Assuming that maltose and erythrogranulose were the sole products of the digest, the yield calculated from the observed R.P. of the digest is 58.8 gm. or 39.5% of the original substrate. In view of the difficulties in the quantitative handling of the material, the difference between calculated and observed yields is hardly significant. Small losses unavoidably occurred at various stages of the procedure.*

This experiment, in conjunction with the foregoing results, thus gives grounds for the statement that the products of β-amylase action on starch are almost exclusively maltose and erythrogranulose, the latter being an unhydrolyzed residue which is precipitated by alcohol of about 50% concentration.

SECTION II. THE ACTION OF α-MALT AMYLASE

1. The Action of α-Amylase on Soluble Starch

The change in reducing power was followed in two series of digests by α-amylase in which starches Nos. 1 and 2 were used as substrate. The enzyme concentration was varied in each series.

Digests 13–15

Total volume—200 ml.; pH, 5.4; starch No. 1—0.985%; enzyme—5,10 and 25 mg. of α-amylase in Digests 13, 14 and 15, respectively.

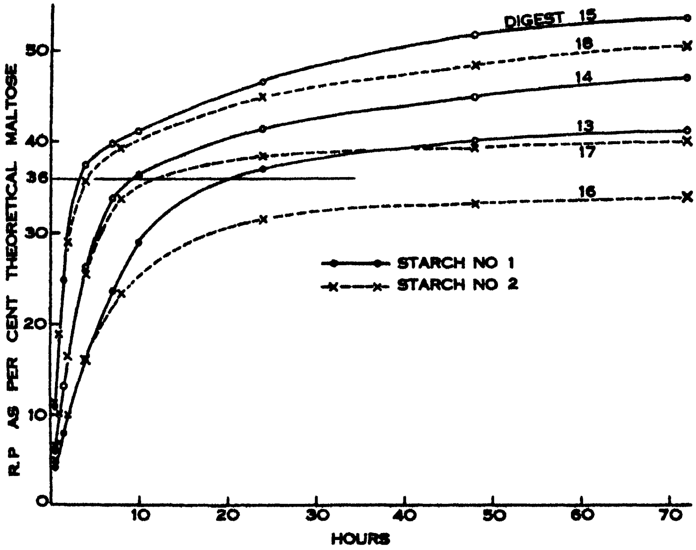

FIG. 1. *Digests 13–18. α-Malt amylase acting on 1% soluble starch (pH 5 4, 35° C.). Digests 13 and 16—5 mg. of enzyme; 14 and 17—10 mg. of enzyme; 15 and 18—25 mg. of enzyme.*

**After the erythrogranulose had been filtered off, the alcoholic mother liquor (52% alcohol) still contained a trace of dissolved material which gave a rose-pink iodine color, as was determined by evaporating 100 ml. to dryness and redissolving the residue in 10 ml. of water. This material was not thrown out by increasing the alcohol concentration to 85%, although a faint turbidity developed.*

Digests 16–18

Total volume—200 ml.; pH, 5.4; starch No. 2—1.022%; enzyme—5, 10 and 25 mg. of α-amylase in Digests 16, 17 and 18, respectively.

R.P. values, determined on 20-ml. samples, were calculated as percentages of the theoretical maltose for complete conversion. As before, no corrections were made for the R.P. of the substrates, and the R.P. of the α-amylase preparation was negligibly small. Progress curves, plotted from the data, are shown in Fig. 1.

The following points are clear:

1. For both substrates (soluble starches Nos. 1 and 2) the degree of hydrolysis is greater with higher enzyme concentration.

2. For a given concentration of enzyme, although the progress curves for the two substrates lie close together initially, they diverge considerably later in the reaction, starch No. 1 being finally hydrolyzed to a greater extent than starch No. 2. This divergence is less marked with higher enzyme concentration.

The first of these features, namely the dependence of the final degree of hydrolysis upon the concentration of α-amylase, is very noticeable in the data reported by van Klinkenberg (12), particularly if the whole of the time/progress data from his Tables VI to X be plotted (12, p. 180). In fact, his final reducing values (and there seems little doubt that the reaction had virtually ceased in all cases by the time the final determination was made) vary from about 14 to 43% of the theoretical R.P. for complete transformation into maltose when the amount of enzyme was varied from 1.66 to 33.3 mg. per 200 ml. digest. The form of these progress curves shows that little reaction occurred in any of the digests after the first 6–10 hr. This fact suggests that the enzyme becomes rapidly inactivated or inhibited in starch digests under van Klinkenberg's conditions ($T = 40°$ C., buffered at pH 5.75 with $N/40$ citrate), a supposition that would explain the widely different apparent limits of saccharification with different enzyme concentrations. It is clear that the same factor is operative under the conditions of Digests 13–18, thus accounting for the different saccharification limits observed with different amounts of enzyme, although under the conditions of these digests ($T = 35°$ C.; pH—5.4; buffered with 0.016 N acetate) the enzyme remains active much longer, there being a rise in R.P. in all cases after 24 hr.

In spite of this factor, which seriously complicates the interpretation of progress curves for low enzyme concentrations (more especially those of van Klinkenberg), the present experiments suggest that after the rapid production of reducing material equivalent in R.P. to 34–37% of the theoretical maltose, there follows a much slower rise in R.P. This seems clear from the fact that digests with 10 and 25 mg. of α-amylase, with both substrates, show noticeable inflections in this region, the inflections occurring when the enzyme is still active.

The results are thus in agreement with those of van Klinkenberg in regard to the general form and characteristics of the progress curves of digests of starch by α-amylase.

Partial Flocculation and Disappearance of Iodine Color

Two further features that have been found to characterize the action of α-amylase on both starch and erythrogranulose are (1) a partial flocculation of the substrate which occurs early in the reaction and (2) the disappearance of the iodine coloration. In Digests 13–18 the times at which flocculation occurred varied from 25–60 min. and the times for the disappearance of the iodine color varied from 60–190 min., both effects being earlier with higher enzyme concentrations.

The onset of flocculation is marked by a sudden change in the appearance of the digest; loose, flocculent aggregates are formed which rapidly settle out, leaving the digest almost water clear, the whole process being completed within a few minutes of its onset. The effect is strictly reproducible; in digests of similar composition the times at which flocculation occurs are consistently the same. In the cases investigated, the dry weight of the precipitated material varies from 3–5% of the total substrate when soluble starch is used, and from 5–9% when erythrogranulose is used, the values depending on the particular starch preparations. It would appear that the flocculation is due to the hydrolytic degradation of a supporting colloid which normally retains this fraction in a stable suspension. Since no flocculation occurs during the selective hydrolysis of the β-starch fraction of soluble starch by β-amylase, it is probable that the material that flocculates is associated with the erythrogranulose fraction of starch, a supposition that is supported by the larger yield of flocculum from the latter.*

The phenomenon of partial flocculation provides an additional distinguishing peculiarity of the action of α-amylase as opposed to β-amylase.

The Effects of Heating Solutions of α-Amylase

van Klinkenberg reports an "activation" of his α-amylase preparation when it is heated for a second time at 70° C. (the enzyme having been previously held at this temperature during its preparation). The effect is peculiar in that the data reported by van Klinkenberg for two progress curves suggest that the heating did not appreciably alter the rate of the reaction until it was in its later stages. In other words, the activation became evident primarily as an increase in the saccharification limit. Several attempts to reproduce this effect with the author's preparation have failed. In all cases the effect of the second heat treatment has been to decrease the activity of the enzyme as judged by both initial velocity and final degree of saccharification. The results of a typical experiment to illustrate this effect are given below.

**This aspect of the action of α-amylase will be discussed in more detail in a subsequent communication.*

A solution of α-amylase, 100 mg. in 100 ml., was prepared. A portion of it was left unheated (Control); the remainder was heated for 14 min. at 70° C. (Heated).

Digests 19–22

Total volume—200 ml.; pH, 5.4; substrate—1.044% of starch No. 2, throughout. Enzyme—Digests 20 and 22—10 and 20 mg. Control enzyme, respectively; Digests 21 and 23—10 and 20 mg. Heated enzyme.

The observations on these digests are shown in Table IV.

TABLE IV

THE EFFECT OF HEATING α-AMYLASE

Digest	α-Amylase	R.P. as percentage theoretical maltose					
		1 hr.	3 hr.	7 hr.	24 hr.	48 hr.	72 hr.
19	10 mg. Control	10 8	23 0	33 6	38 7	39 9	39 8
20	10 mg. Heated	6 2	11 5	19 4	31 1	34 0	34.3
21	20 mg. Control	17 2	32 8	38 6	43 3	44 7	44.7
22	20 mg. Heated	9 0	18 5	30 0	38 4	40.4	40.6

With both enzyme concentrations, it is clear that a partial inactivation of the α-amylase has resulted from the heat treatment, both the initial velocity and the final saccharification value being decreased. In this particular respect, therefore, the properties of the author's preparation appear different from those of van Klinkenberg's.

SECTION III. THE HYDROLYSIS OF ERYTHROGRANULOSE

Erythrogranulose, the non-reducing residue that is left after the completed action of β-amylase on soluble starch, is not attacked by this enzyme after its isolation. Prolonged treatment with large amounts of β-amylase results in the appearance of mere traces of reducing material and the iodine color remains unchanged (*cf.* Digest 34, p. 204). It is readily attacked by α-amylase with the production of reducing material; a partial flocculation occurs early in the reaction, and the iodine coloration undergoes a sequence of changes from blue-violet, through mauve, rose, and pale brown, leading finally to complete absence of coloration.

According to van Klinkenberg's hypothesis, the action of α-amylase on soluble starch is interpreted as consisting initially of the complete hydrolysis of erythrogranulose to maltose, with no appreciable hydrolysis of the β-starch fraction. The hypothesis implies, therefore, (1) that erythrogranulose is completely transformed into maltose by α-amylase, and (2) that the α-amylase exerts a selective action on the erythrogranulose fraction of starch. The experiments that will be described in the first three parts of this section combine to show that both of these assumptions are untenable.

1. *The Saccharification Limit of α-Amylase Acting on Erythrogranulose*

The progress of reducing power in a large number of digests of erythrogranulose by α-amylase has been followed. The records of a typical series of digests will be considered.

Digests 23, 24 and 25

Enzyme; 5, 10 and 25 mg. α-amylase, respectively; total volume—200 ml.; substrate—1.00% erythrogranulose; pH, 5.4, throughout.

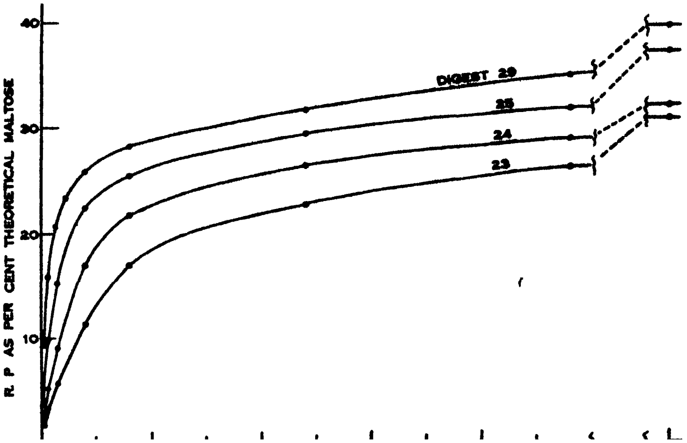

FIG. 2. *Digests 23, 24, 25 and 29. α-Malt amylase acting on erythrogranulose (pH 5 4, 35° C.). Digests 23, 24, 25 with 5, 10 and 25 mg. of enzyme, respectively, and 1% of substrate; Digest 29 with 40 mg. of enzyme and 0 36% of substrate.*

Progress curves are shown in Fig. 2, the R.P. values being expressed as percentages of the theoretical maltose (211 mg. per 20 ml.). In Digests 23, 24 and 25, partial flocculation occurred after 80, 57 and 34 min., respectively, and the iodine coloration disappeared after 260, 190 and 150 min., respectively.

It will be seen that, as in the action of α-amylase on soluble starch, there is no sharp saccharification limit, the final values of R.P. being somewhat greater with increasing enzyme concentration. For comparison, the progress curve of Digest 29 (page 199) has been plotted in Fig. 2; in this digest the concentration of erythrogranulose was reduced to 0.36%, while the amount of enzyme was increased to 40 mg., the enzyme/substrate ratio thus being increased fivefold as compared with Digest 25. It will be seen that the final degree of saccharification in Digest 29 (40.0% R.P. of theoretical maltose) is only slightly greater than that for Digest 25 (37.6%).

It is clear from this experiment that α-amylase does not effect the quantitative conversion of erythrogranulose into maltose; the R.P. of the products corresponds to only a little more than one-third of the R.P. of the theoretical amount of maltose.

2. *Comparison of the Action of α-Amylase on 1.00% Soluble Starch and 0.36% Erythrogranulose*

Observations were made on parallel digests of 1.00% of starch No. 2 and 0.36% of erythrogranulose, for two concentrations of α-amylase. The digests of starch can be regarded as containing 0.36% of erythrogranulose plus 0.64% of β-starch[*], whereas the digests of erythrogranulose contain 0.36% of erythrogranulose and no β-starch. If, as is postulated by van Klinkenberg, α-amylase acts selectively on erythrogranulose it would be expected that similar amounts of reducing material would be formed from the two substrates.[†]

Digests 26–29

Total volume—200 ml.; pH, 5.4, throughout. Digests 26 and 27—1.00% of starch No. 2; 10 mg. and 40 mg. α-amylase, respectively. Digests 28 and 29—0.36% of erythrogranulose; 10 mg. and 40 mg. α-amylase, respectively.

The observations are recorded in Table V. The R.P. values have been expressed both in absolute values (as mg. of maltose per 20 ml.) and as percentages of the theoretical maltose (211 mg. per 20 ml. for the starch digests, and 76 mg. per 20 ml. for erythrogranulose).

TABLE V

ACTION OF α-AMYLASE ON STARCH AND ERYTHROGRANULOSE

Digest	26		27		28		29	
α-Amylase	10 mg.		40 mg.		10 mg.		40 mg.	
Substrate	1.00% Starch No. 2				0.36% Erythrogranulose			
Hr.	R.P. as mg. maltose per 20 ml. and as percentage theoretical maltose							
0.25	9.6 mg.	*4.5%*	19.7 mg.	*9.3%*	3.0 mg.	*3.9%*	7.1 mg.	*9.3%*
0.6	14.8	*7.0*	32.4	*17.4*	5.7	*7.5*	12.1	*15.9*
1.3	23.6	*11.2*	52.9	*25.1*	9.8	*12.9*	15.7	*20.7*
2.25	34.5	*16.3*	66.9	*31.7*	13.1	*17.2*	17.8	*23.4*
4.0	50.2	*23.8*	75.4	*35.7*	15.9	*21.0*	19.7	*25.9*
8.0	67.5	*32.0*	82.6	*39.1*	18.1	*23.8*	21.5	*28.3*
24.0	79.0	*37.4*	92.8	*44.0*	20.9	*27.5*	24.1	*31.8*
48.0	83.5	*39.6*	104.0	*49.3*	22.5	*29.6*	26.7	*35.2*
193.0	88.9	*42.1*	125.2	*59.4*	24.3	*32.0*	30.4	*40.0*
Flocculation time, min.	47		31		50		32	
Disappearance iodine color (approx.), min.	165		145		175		145	

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[*] *The author has adopted van Klinkenberg's estimate of the proportions of the two components for the purposes of this experiment. It is in close agreement with the author's values for this particular preparation (see page 190).*

[†] *The slow transformation of β-starch into erythrogranulose which is postulated by van Klinkenberg need not be considered in the present argument, since according to his hypothesis this would not be appreciable until after the R.P. of starch digests has attained a value of about 36% theoretical maltose. (See also page 202).*

The degree of hydrolysis of the two substrates (as judged by the R.P. expressed as percentage theoretical maltose) is approximately the same during the early part of the reaction in digests with equal enzyme concentration. (Compare values for Digests 26 and 28, and Digests 27 and 29.) Subsequently the degree of hydrolysis of starch is greater than that of erythrogranulose. This militates against the view that the initial action of the enzyme on starch is a selective hydrolysis of erythrogranulose.

In Fig. 3 are plotted the absolute values of R.P. (expressed as mg. of maltose per 20 ml.). It will be seen that from the beginning of the reaction the absolute R.P. of the digests of starch greatly exceeds that of the corresponding digests of erythrogranulose. It is clear, therefore, that a large part of the reducing material in the starch digests arises from the hydrolysis of the β-starch fraction, since all the digests contain the same concentration of erythrogranulose.

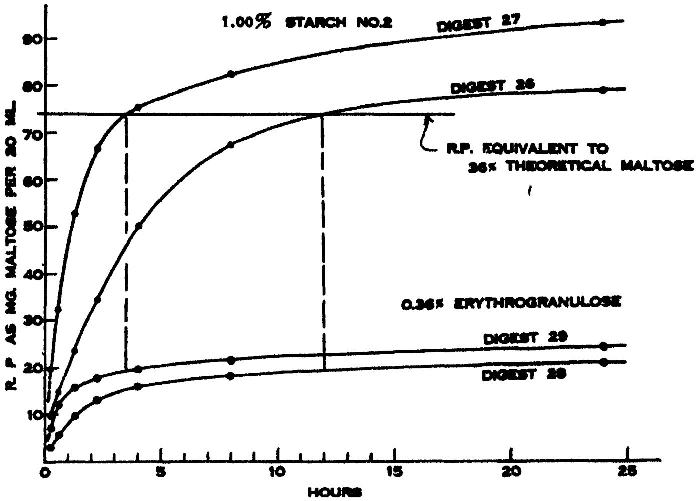

FIG. 3. *Comparison of the action of α-malt amylase on 1% soluble starch and 0.36% erythrogranulose. Digests 26 and 27—1.00% of starch No. 2, with 10 mg. and 40 mg. of enzyme, respectively; Digests 28 and 29—0.36% erythrogranulose, with 10 mg. and 40 mg. of enzyme, respectively.*

The forms of the progress curves of the starch digests are typical of those that have been discussed earlier; Digest 27, with high enzyme concentration, exhibits the feature that has been emphasized by van Klinkenberg (and which is the foundation for his view regarding the selective action of α-amylase on erythrogranulose), namely, a well defined inflection when the R.P. has reached a value corresponding to about 36% theoretical maltose (73.9 mg. of maltose); Digest 26, as is typical with low enzyme concentration, shows no noticeable inflection, but hydrolysis after this value is reached is extremely slow. The times required for the R.P. to reach this level (=73.9 mg. of maltose per 20 ml.) in Digests 27 and 26 were 3.4 and 12 hr., respectively. At these times the R.P. of the corresponding digests of erythrogranulose were equivalent to only 19.1 and 19.0 mg. of maltose per 20 ml. respectively (Digest 29 at 3.4 hr.; Digest 28 at 12 hr.). From this it follows that when the R.P. of starch digests by α-amylase reaches a value corresponding to 36% of the theoretical maltose only a small fraction (about one-quarter) of the R.P. is due to products of erythrogranulose breakdown, the bulk of it (about three-quarters) being due to products of the action of α-amylase on the β-starch fraction; it would appear, from the experiment, moreover, that the proportion is (within wide limits) independent of the enzyme concentration. There remain, therefore, no grounds for believing that α-amylase exerts a selective hydrolytic action on erythrogranulose. Reducing material is also produced by the hydrolysis of the β-starch fraction, although it is to be noted that this fraction is not quantitatively transformed into maltose, as occurs under the action of β-amylase.

At this point a possible objection to the nature of the experiment described above should be considered. The view might be advanced that the erythrogranulose substrate as used in these digests may be more resistant to hydrolysis by α-amylase than erythrogranulose, as it occurs normally as a constituent of starch, having possibly become altered in the course of its isolation. Several facts, however, stand opposed to this supposition. In the first place, experiments have been carried out on the hydrolysis of erythrogranulose without isolating it from the original starch digest in which (by allowing β-amylase to act to completion) it was freed from β-starch. Portions of such completed β-amylase digests, containing erythrogranulose and maltose, have been used as a source of erythrogranulose substrate for α-amylase digests; in some cases the β-amylase of the original digest was destroyed by heating to 70° C. for half an hour, in others it remained active. We thus studied the action of α-amylase alone, and the joint action of α- and β-amylases on erythrogranulose that had not been subjected to the conditions of the isolation procedure. The rates of hydrolysis and the final degrees of saccharification in such digests were the same as in digests of "isolated" erythrogranulose under the same conditions. It became clear, therefore, that the precipitations with alcohol and the subsequent dehydration with alcohol and ether do not cause any appreciable change in erythrogranulose. Other considerations suggest that the hydrolysis of isolated erythrogranulose proceeds at approximately the same rate as that of erythrogranulose present in its natural association with β-starch. In Table V (bottom) it will be seen that the times at which partial flocculation occurred were approximately the same in each pair of digests with the same enzyme concentration. As has been mentioned above (p. 196), this partial flocculation is a phenomenon associated with the degradation of erythrogranulose by α-amylase; accordingly the close synchronization of this event in digests of isolated erythrogranulose and erythrogranulose present as a starch constituent would appear to constitute good evidence that erythrogranulose is degraded at similar rates in these different states.

3. *Examination by the Yeast Methods of Digests by α-Amylase*

Observations on two digests, of soluble starch and erythrogranulose, respectively, will first be considered.

Digests 30 and 31

Total volume—200 ml.; pH, 5.4; 10 mg. α-amylase. Substrates—Digest 30—0.500% starch No. 1; Digest 31—0.500% erythrogranulose.

After 18.7 hr. the reductions determined by the Macro-Copper method on 20-ml. samples were equivalent to 44.9 mg. maltose (Digest 30) and 33.1 mg. (Digest 31), corresponding to 42.6 and 31.4% of theoretical maltose for starch and erythrogranulose, respectively. At this time 5-ml. samples of the digests were heated at 100° C. for five minutes and diluted to 100 ml. for examination by the yeast methods. In addition, solutions of the substrates were analyzed; the erythrogranulose at the concentration of the diluted sample showed no reducing power, while the starch solution showed a low reducing power, which, calculated to an equivalent concentration, will be used to correct the results for the sample of Digest 31. The results were as shown in Table VI.

TABLE VI

RESULTS OF EXAMINATION BY THE YEAST METHOD

—		R.P. (in ml. $N/200$ thiosulphate per 2 ml. digest diluted 20 times)		
		Total R.P.	After *M. krusei*	After *M. tropicalis*
Digest 30	Digest of 0 5% starch	0 78	0 69	0 11
	0 5% Starch before hydrolysis	0 05	0 03	0 02
	Products of hydrolysis of 0 5% starch	0 73	0 66	0 09
Digest 31	Digest of 0 5% erythrogranulose	0 55	0 48	0 20

These observations show clearly that the products of the action of α-amylase do not consist exclusively of maltose, whether the enzyme acts on starch or on erythrogranulose. In addition to a small amount of glucose (indicated by the slight but significant removal by *M. krusei*) a fraction of the R.P. is not removed by *M. tropicalis*. This non-removable, and therefore non-maltose fraction accounts for 12% of the R.P. in the starch digest and 36% in the erythrogranulose.

These values suggest that the non-removable reducing material is formed exclusively from the erythrogranulose fraction of starch. It was shown in Section I that starch No. 1 contains 60% of β-starch and 40% of erythrogranulose. The reducing substances in Digest 30 may therefore be considered to have arisen from the hydrolysis of 0.3% of β-starch and 0.2% of erythrogranulose. The non-removable reducing fraction of this digest had an R.P. of 0.09 cc. $N/200$ thiosulphate (per 2 ml. of diluted digest). From the results of Digest 31 (0.5% of erythrogranulose) we would expect the R.P. of non-removable reducing products from 0.2% of erythrogranulose to be $0.4 \times .20 = 0.08$ cc. $N/200$ thiosulphate (per 2 ml. of diluted digest). It would appear, therefore, that the non-removable reducing fraction arises only from the breakdown of erythrogranulose by α-amylase, and that the reducing products of its action on β-starch are entirely removed by *M. tropicalis*. This conclusion that different products arise from the two starch components is supported by the observations of other workers (5, 6, 8). It constitutes strong evidence against the transformation of β-starch into erythrogranulose which is postulated by van Klinkenberg to explain the slow rise in R.P. observed in the later stages of starch digests by α-amylase.

The appearance of the non-removable reducing fraction was followed during the early stages of a digest of erythrogranulose.

Digest 32

Composition similar in all respects to Digest 31.

Samples (5 ml.) were withdrawn at intervals, heated five minutes at 100° C., and diluted to 50 ml. for examination. The substrate alone at similar dilution showed a negligibly small R.P. (0.02, 0.01 ml. *N*/200 thiosulphate per 2 ml.). The results are given in Table VII, the R.P. being expressed in ml. *N*/200 thiosulphate per 2 ml. of digest of 1/10 strength. The observations on Digest 31 are also included.

TABLE VII

ACTION OF α-AMYLASE ON ERYTHROGRANULOSE, FOLLOWED BY YEAST REMOVAL METHOD

Time	R.P. in ml. *N*/200 thiosulphate per 2 ml. Digest (1/10 strength)			
	Total R.P.	After *M. krusei*	After *M. tropicalis*	Removed by *M. tropicalis*
10 min.	0 10	—	0 10	0 00
30 min.	0 22	—	0 17	0 05
1 hr.	0 35	—	0 20	0 15
2 hr.	0 71	0 69	0 24	0 47
18 7 hr. (Digest 31)	1 10	0 96	0 40	0 70

These data have been plotted in Fig. 4, from which it will be seen that early in the reaction the non-removable fraction preponderates, there being

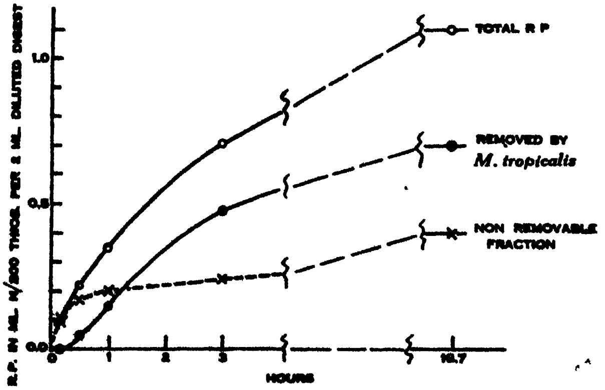

FIG. 4. *Action of α-malt amylase on erythrogranulose. Progress curves based on the yeast removal method.*

an initial lag in the appearance of removable reducing material. After 1.3 hr. the R.P. of the two fractions are equal, after which the R.P. of removable reducing material predominates. It can be concluded, therefore, that maltose is not produced in the first stage of the hydrolysis of erythrogranulose, since the earliest detectable reducing material is not removed by *M. tropicalis.* By the end of half an hour, however, maltose is present in measurable concentration, after which it increases rapidly. It would appear that glucose is not formed in significant amounts until after three hours.

One point in connection with the non-removable reducing fraction of the products of α-amylase action on starch and erythrogranulose deserves mention here. In view of statements by previous workers that the presence of dextrins decreases the rate of fermentation of maltose by yeast, it was conceivable that under the standard yeast removal conditions (see p. 187) a complete removal of maltose was not being achieved. Accordingly, samples of several digests were subjected to more rigorous removal treatments; in some cases, the time of inoculation with *M. tropicalis* was prolonged to one hour; in others, samples were subjected to successive incubations with two (and in one case, three) fresh batches of yeast. In no case was there an increase in the removal by the yeast, the values for the residual R.P. being the same within the experimental error as those obtained using the standard Harding and Nicholson conditions.

4. *The Joint Action of α- and β-Amylases on Erythrogranulose*

Observations by van Klinkenberg (11, p. 266) showed clearly that β-amylase is able to hydrolyze certain of the products of degradation of erythrogranulose by α-amylase. This phenomenon (which is difficult to reconcile with his view that erythrogranulose is transformed into 100% maltose by α-amylase) has been studied in order to determine at what stage in the breakdown, material hydrolyzable by β-amylase appears. Accordingly digests of erythrogranulose with α-amylase alone, β-amylase alone and with the two enzymes together were followed.

Digests 34–36

Total volume—200 ml.; pH, 5.4; 0.500% of erythrogranulose, throughout. Enzyme: Digest 34—6 mg. β-amylase; Digest 35—10 mg. α-amylase; Digest 36—6 mg. β- + 10 mg. α-amylase.

The observations are shown in Table VIII. The R.P. values, corrected for the slight R.P. of the β-amylase preparation in Digests 34 and 36 are expressed as mg. maltose per 10 ml.

Progress curves for these digests are shown in Fig. 5.

Digest 34 illustrates the typical failure of β-amylase to produce more than a mere trace of reducing material from erythrogranulose. There was no change in iodine coloration, nor did flocculation occur.

Digest 35 shows the usual increase in R.P. during the breakdown of erythrogranulose, the value attained at 26 hr. corresponding to 33.6% of the

TABLE VIII

SEPARATE AND JOINT ACTION OF α- AND β-AMYLASES ON ERYTHROGRANULOSE

Digest	34	35	36
Enzyme	β-Amylase	α-Amylase	α + β-Amylase
Time, hr.	R.P. expressed as mg. maltose per 10 ml.		
0.5	0.2	3.7	8.4
1.17	0.3	7.7	14.7
2.17	0.3	10.6	17.5
4.42	0.4	13.0	20.1
7.42	0.3	14.1	21.3
20.4	0.3	16.5	23.0
26.0	0.3	16.8	23.2
Flocculation time, min.	No flocculation	50	52
Disappearance iodine color, min.	No change	120–130	120–130

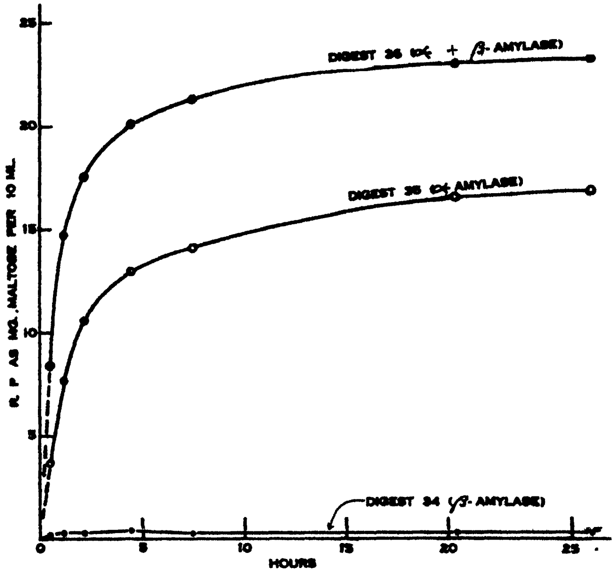

FIG. 5. *Digests 34-36. Separate and joint action of α- and β-malt amylases on 0.5% erythrogranulose.*

theoretical maltose. Flocculation occurred 50 min. after the beginning of the reaction. The weight of the flocculum (determined on 50 ml. of the digest after shaking it) was 5.5% of the total substrate.

Digest 36 shows that from the earliest observed stages the presence of β-amylase with α-amylase results in a considerably increased R.P., the final value being approximately 40% greater than that in Digest 35. Flocculation occurred 52 min. after the beginning of the reaction. The weight of flocculum was 5.2% of the original substrate.

From this experiment it is clear that, although β-amylase has no appreciable action on intact erythrogranulose, yet once hydrolysis by α-amylase has begun, β-amylase rapidly hydrolyzes certain of the degradation products. This secondary hydrolysis by β-amylase does not appreciably alter the time at which flocculation occurs nor the weight of the flocculum; nor is the rate of disappearance of the iodine coloration changed. These phenomena would, therefore, appear to be conditioned only by the primary degradation by α-amylase.

Discussion

The experiments that have been described confirm in essential respects the observations of van Klinkenberg (10–13) concerning the action of α- and β-malt amylase. Extension of the range of experiment, however, and the introduction of the yeast removal method for the fractionation of reducing products leads to a different interpretation of some of the observed effects, and consequently, to a considerably modified view of their bearing on the problem of starch constitution.

The results with β-amylase described in Section I are in accord with those of van Klinkenberg (and various earlier authors) in showing that this enzyme selectively hydrolyzes a portion of the starch substance, transforming it almost exclusively into maltose; the residual material (Wijsman's erythrogranulose) is non-reducing and gives a blue or violet iodine coloration depending on its concentration. It is convenient to designate as β-starch that fraction of starch that is selectively hydrolyzed by β-amylase (in accordance with van Klinkenberg's nomenclature). The relative proportions of these two fractions of starch, as determined by van Klinkenberg for a soluble potato starch prepared by a modified Lintner procedure, were 64 parts of β-starch to 36 parts of erythrogranulose. The author has been able to confirm these values, using a soluble starch prepared according to van Klinkenberg's method, but has found, however, that starch solubilized by this method possesses considerable reducing power for which no adequate correction can be made in assessing the saccharification limit of β-amylase. The author, therefore, is inclined to regard as more reliable, determinations made on a soluble potato starch, prepared according to Small's (9) procedure, which had a considerably lower reducing power and at the same time gave a highly dispersed "solution". The results with this substrate would indicate the presence of about 60–61% of β-starch and 39–40% of erythrogranulose.

With regard to the action of α-amylase, the author's views diverge considerably from those of van Klinkenberg. The experiments described in Section II confirm the observation of van Klinkenberg that when α-amylase (in sufficient concentration) is allowed to act on soluble starch, the reducing power rises rapidly until it attains a value equivalent to 34–38% of the theoretical maltose for complete conversion, after which the reducing power continues to rise but at a considerably slower rate. van Klinkenberg interprets the initial rapid production of reducing material as being due to the selective and complete hydrolysis of erythrogranulose to maltose, and he suggests that the subsequent slow hydrolysis is due to a slow transformation of the residual β-starch into erythrogranulose, which is hydrolyzed as it is formed.

The experiments described in Section III appear to render this view untenable. These experiments show that α-amylase does not selectively hydrolyze the erythrogranulose fraction of starch, but that from the beginning of the reaction the greater part of reducing material arises from the hydrolysis of the β-starch fraction. The evidence may be summarized briefly as follows:

1. Several observations prove conclusively that erythrogranulose is not converted quantitatively into maltose by α-amylase:

(*a*) After prolonged digestion with large amounts of the enzyme, the reducing power of the products corresponds to not more than about 40% of the theoretical maltose.

(*b*) Approximately one-third of the reducing power of the products is due to material that is not removed by *M. tropicalis*, and is therefore not maltose (or glucose). This non-removable reducing material is also formed in digests of soluble starch in amounts that suggest that it arises exclusively from the hydrolysis of the erythrogranulose fraction.

(*c*) Certain of the products of α-amylase action on erythrogranulose are rapidly hydrolyzed by β-amylase and are therefore not maltose.

(2) By comparing the rates of appearance of reducing material under similar conditions from 1.00% of starch and 0.36% of erythrogranulose, it was shown that the action of α-amylase on soluble starch is not a selective hydrolysis of the erythrogranulose fraction. The reducing power of the starch digests greatly exceeded that of the corresponding erythrogranulose digests from the beginning of the reaction (although the two substrates contained approximately the same amount of erythrogranulose).

We are thus lead to abandon the hypothesis of van Klinkenberg, according to which starch is regarded as consisting of two components that are hydrolyzed specifically by the two malt amylases. There is no doubt that β-amylase, in isolation, selectively hydrolyzes one fraction of starch (β-starch), transforming it almost exclusively into maltose, and leaves an unhydrolyzed residual fraction (erythrogranulose). It is equally clear, however, that α-amylase does not selectively hydrolyze the erythrogranulose fraction of starch, but that from the beginning of its action on soluble starch, reducing substances are produced from both the β-starch and erythrogranulose fractions.

In the simultaneous action of α- and β-amylases on soluble starch we would picture the degradation as taking place in the following manner. From the beginning of the reaction the β-starch fraction would be acted upon by both α- and β-amylases; there is little doubt that the greater part of its hydrolysis would be effected by β-amylase, since only this enzyme is able to bring about a quantitative conversion into maltose (see p. 194). The hydrolysis of the erythrogranulose portion of the substrate would be initiated by α-amylase but the products of this primary breakdown would be then further hydrolyzed by β-amylase. This question will be further considered in a subsequent communication which will deal with the fractionation and characterization of the products of α-amylase. Finally, it should be pointed out that although it is possible to obtain a sharp fractionation of the starch substance by the action of β-amylase, it cannot be held to be proved that the two fractions demonstrable by this means pre-exist as separate entities in starch, and the possibility must be recognized that they may represent fragments of a single molecule.

Acknowledgments

The author wishes to record his indebtedness to the late Prof. V. J. Harding and to Dr. T. F. Nicholson for making possible the use of their yeast removal methods in this investigation, and also to gratefully acknowledge the careful technical assistance of Mr. James Alexander.

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STUDIES ON THE SYSTEM CALCIUM-OXIDE–SULPHUR-DIOXIDE–WATER

I. DETERMINATION OF VAPOR PRESSURES AND CONDUCTIVITIES[1]

By G. W. Gurd[2], P. E. Gishler[3] and O. Maass[4]

Abstract

The system calcium-oxide–sulphur-dioxide–water is to be investigated in order to determine the nature of existing equilibria, and the way in which these vary with concentration and temperature. In this paper a technique is described by means of which vapor pressures and conductivities have been measured over the temperature range 25° to 130° C. and over the concentration range 0 to 2 5% CaO and 0 to 6% SO_2. The data obtained are systematized in tabular form.

The system calcium-oxide–sulphur-dioxide–water is of considerable theoretical interest. It has been assumed that calcium sulphite is first formed and that with subsequent addition of sulphur dioxide the calcium sulphite dissolves owing to the formation of calcium bisulphite. At the time when this investigation was first started there were no data available from which quantitative conclusions could be drawn regarding the existence of calcium bisulphite, and the nature of the equilibria in this three component system. Nothing was known regarding the magnitude of the hydrogen ion concentration at various temperatures and concentrations.

Apart from the academic interest attached to the system calcium-oxide–sulphur-dioxide–water, a knowledge of the nature of the equilibria and especially of the hydrogen ion concentration is of utmost importance in connection with the mechanism of the sulphite cooking of wood. As a start in the investigation, the system sulphur-dioxide–water has been thoroughly examined (1, 6, 7), and the interesting conclusion was drawn that with rise in temperature the equilibrium $SO_2 + H_2O \leftrightharpoons H_2SO_3$ is shifted to the left, so that the apparent "strength" of sulphurous acid decreases with rise in temperature.

Sulphurous acid of 4% concentration at 140° C. (the temperature at which the sulphite cook is carried out) has a hydrogen ion concentration of only 0.002%. With the addition of calcium oxide this is still further reduced, but not nearly to the extent to which one might be led to believe by the unexpectedly low hydrogen ion concentration of sulphurous acid at that temperature.

As a first step towards the determination of the exact relations obtaining in sulphite liquor, Gurd and Maass (5) in 1930 started with the measurement

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of vapor pressures and conductivities. In 1933 Gishler and Maass repeated some of the measurements and completed the desired range of concentrations to obtain the necessary data.

This paper deals with a description of the technique employed in the measurement of vapor pressures and conductivities of the system over the temperature range 25° to 130° C. and the concentration range 0 to 2.5% CaO and 0 to 6% SO_2. The data obtained are systematized in tables so as to make it available in a useful form, because especially the vapor pressures are of interest to the pulp and paper industry. In a subsequent paper the conclusions drawn from these data and the calculation of the hydrogen ion concentration will be given. Further papers on precipitation temperatures of the system and the influence of the presence of lignin and cellulose will follow.

Recently a paper was published (2) on the measurement of the vapor pressures of calcium-oxide–sulphur-dioxide–water solutions over the temperature range 0° to 37° C. This range has been covered by Grieve and Maass (4), and the conductivities have been measured as well. A paper on this phase of the investigation will be published shortly.

Experimental

The technique that was devised for this work had for its object the bringing together of the desired amounts of pure calcium oxide, sulphur dioxide and water in such a way as to ensure the absence of oxygen, carbon dioxide and inert gases, and yet give an accurate measure of concentration. With this in view, the experiments were carried out in such a way that the concentration of the sulphur dioxide in the liquid phase could be accurately estimated. Furthermore, special attention was paid to ensure the establishment of true equilibrium in the liquid phase, since the system is of such a nature that there is grave danger of wrong results being obtained, owing to a lag in establishing uniform distribution throughout the liquid phase and a proper equilibrium between the solid and liquid, and liquid and vapor phases.

The apparatus for the measurement of the vapor pressures and conductivities is shown in Fig. 1. A high-pressure cylinder containing sulphur dioxide free from sulphur trioxide was connected through a phosphorus pentoxide drying tube to four bulbs, B_1, B_2, B_3, and B_4 in series. These bulbs served to further purify the sulphur dioxide. The volumes of the two measuring bulbs, E_1 and E_2, were accurately determined. They were connected by means of glass tubing of known volume to a two-armed mercury manometer, M. The bulbs were immersed in a water bath to prevent sudden fluctuations of temperature. A tiny bulb, D, bounded by stopcocks S_3 and S_4 served to condense the measured quantity of sulphur dioxide before it was introduced into the reaction cell. The gas-measuring system was connected to the reaction cell through a frozen mercury seal as shown in Fig. 1.

The reaction cell, F, was made of 1 in. Pyrex tubing, and its volume was approximately 95 cc. The calcium oxide and water were introduced into the cell through two side arms near the top.

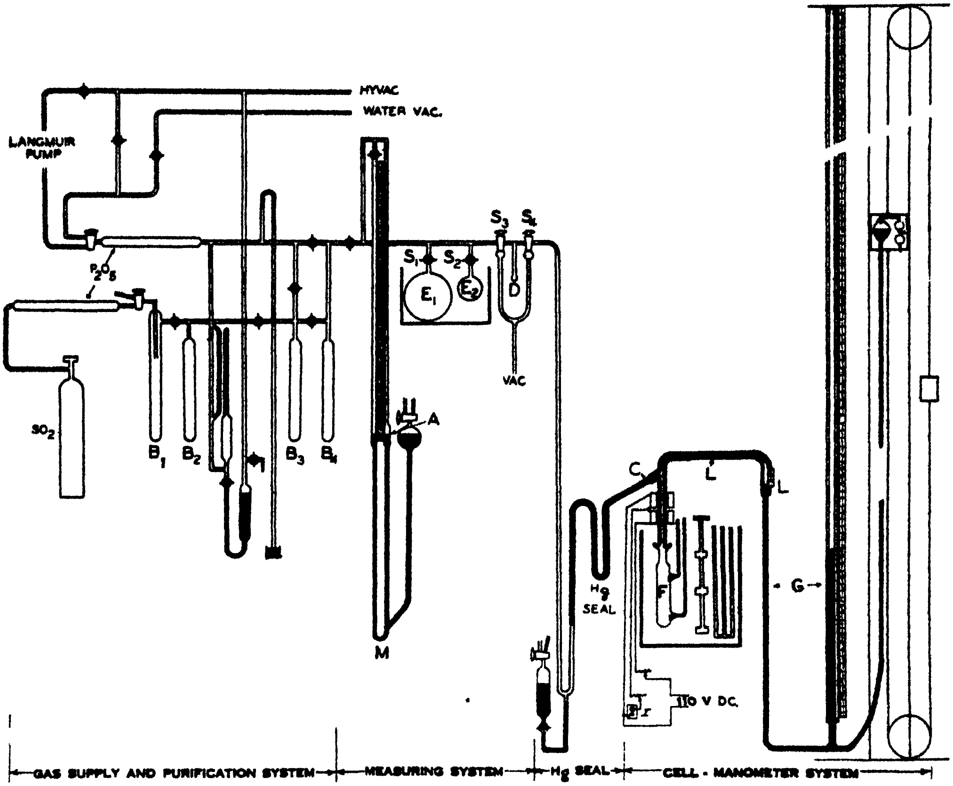

FIG. 1. *Apparatus for the purification and measurement of sulphur dioxide, and for the determination of vapor pressures and conductivities of the system calcium-oxide-sulphur-dioxide-water.*

The reagents were stirred by means of an all glass magnetic stirrer. The upper end of the stirrer fitted loosely into the tubing leading from the reaction cell to the manometer. An iron core was sealed into the upper end of the stem. This was surrounded by a double solenoid, one part of which held the stirrer off the bottom; the other part was connected to a make-and-break device which governed the amount of stirring.

Two "bay windows", blown into the side of the cell, contained the platinum electrodes. Each electrode consisted essentially of a strip of $\frac{3}{16}$ in. platinum foil sealed into a $\frac{1}{4}$ in. Pyrex tube. The protruding $\frac{1}{2}$ in. of platinum was securely sealed to the glass tube. The resistance of the solution was measured by means of the ordinary bridge hook-up containing a standard resistance and a Kohlrausch slidewire. The current was supplied by means of a Vreeland oscillator. The null point was determined with ear phones.

Vapor pressures were measured by means of a large, constant-level, closed-end manometer, *G*, capable of measuring pressures as high as 100 lb. per sq. in. A calibrated wooden scale was firmly attached to the manometer support. The manometer tube was air jacketed to prevent sudden fluctuations in temperature. The temperatures of the mercury and of the air above it were determined with a series of thermometers suspended at convenient points. The volume of the manometer tube per unit scale reading was accurately known throughout its entire length. The constant of the manometer was carefully determined.

A well lagged capillary tube, *L*, wrapped with resistance wire, connected the reaction cell to the manometer. High-pressure measurements were made possible by building up an air pressure above the mercury in the manometer bulb by means of a bicycle pump.

In order to obtain accurate vapor pressure data it was necessary to use calcium oxide free from calcium carbonate. This was prepared by grinding clear select crystals of Iceland spar into a fine powder and subjecting it to a temperature of 1000° C. for a week in the presence of a current of dry air free from carbon dioxide. The purity of the calcium oxide (absence of carbonate) was tested by two methods. (i) Some calcium oxide was placed in a test tube containing pure water, hydrochloric acid was added and a stream of air was bubbled through the resulting solution into a clear solution of barium hydroxide. (ii) A small sample of calcium oxide was placed on a microscope slide and covered with a warm solution of gelatin. The slide was immediately chilled, causing the gelatin to set. A drop of hydrochloric acid was placed on the gelatin and it was examined with a microscope. The hydrochloric acid diffused through the gelatin and if carbonate was present tiny bubbles of carbon dioxide were formed.

After pure calcium oxide was obtained it was stored in a vacuum desiccator containing sodium hydroxide and phosphorus pentoxide.

When a solution was to be prepared the cell was thoroughly cleaned and sealed to the system as shown in Fig. 1. One side arm of the cell was sealed. The other was sealed to a 500 cc. empty distilling flask (not shown in the diagram) which was subsequently to be used for removing dissolved gases from the water. The cell and flask were evacuated and then filled with dry air free from carbon dioxide. The side arm was broken and a weighed amount of calcium oxide introduced. The side arm was then sealed about an inch from the cell. The top stem of the distilling flask was broken and a weighed amount of water introduced. The stem was sealed and the water rapidly frozen by surrounding the flask with a freezing mixture of solid carbon dioxide in acetone. The flask and cell were then thoroughly evacuated and mercury was run part way up the mercury seal in order to isolate the cell system. The loss of water during evacuation was negligible, owing to the extremely low vapor pressure of ice at that temperature.

In order to remove dissolved gases the freezing mixture was removed; as the ice melted, the dissolved gases passed into the space above the water. After the ice had melted, the flask was once more surrounded with the freezing mixture. Any water that had passed into the vapor phase was recondensed, whereas very little of the escaped gases would redissolve at that low pressure. Time was allowed for the water to freeze before the gases were removed by evacuation. Three repetitions removed all gases. The water was then distilled into the reaction cell and the distilling flask sealed from the cell. The mercury seal served to isolate this part of the apparatus.

The final step involved the purification, measurement and introduction of sulphur dioxide. The necessary apparatus was evacuated and flushed with sulphur dioxide. B_1 was surrounded with a freezing mixture and the required amount of sulphur dioxide condensed from the storage cylinder. Distillation of the sulphur dioxide into B_2, then into B_3 and finally into B_4, with rejection of the top and bottom fractions, in each case, yielded the pure gas.

The desired amount of sulphur dioxide was allowed to evaporate into the previously evacuated measuring bulbs, E_1 and E_2. The mercury was brought to the fixed 2 cm. level in the right arm of the manometer M and the difference in mercury levels noted. The necessary temperature correction was made. The temperatures of the bulbs and connecting tubing were then read. The weight of sulphur dioxide could then be determined. The sulphur dioxide was condensed from the measuring system into the tiny bulb D by surrounding the latter with a freezing mixture. On opening D to the reaction cell and removing the freezing mixture, the gas passed into the reaction cell. Solution was facilitated by vigorous stirring. When solution was complete, mercury was run into the capillary of the mercury seal, where it was surrounded with solid carbon dioxide in acetone, thus serving as a pressure seal. Any sulphur dioxide remaining in the connecting tubing was condensed in D, from whence it was allowed to expand into the measuring system to be measured. The small amount remaining in the tubing was calculated.

Some experiments were carried on in which there was not sufficient sulphur dioxide to completely dissolve the calcium oxide present. Equilibrium under these circumstances was established slowly, especially at room temperature. The mixture was therefore stirred for approximately 48 hr. before conductivity and vapor pressure determinations were made. It was necessary to keep the lagged tubing between the cell and manometer at a temperature greater than that of the cell in order to prevent condensation of water vapor. The temperature of the cell was regulated to within 0.05° C. by immersing it in a bath of dibutyl phthalate containing the necessary stirrers and heaters. During an experiment, the level of the mercury in the side arm of the manometer was kept as close as possible to zero on the scale, L, by raising and lowering the large mercury bulb which was attached to a pulley device.

When equilibrium had been established the mercury levels were noted and also the temperatures of the bath, the lagged tubing above the cell, and the jacketed space about the manometer tube. To obtain conductivity data the Vreeland oscillator was started, the resistance of the cell was roughly balanced against a standard resistance and the null point obtained on the Kohlrausch slidewire with the aid of ear phones. Vapor pressure and conductivity measurements were made at intervals of approximately 15° C. in the temperature range 25° to 130° C.

After an experiment, a further addition of approximately 1% of sulphur dioxide was made, and a second series of vapor pressure and conductivity measurements carried out. Successive additions and determinations were made until the concentration was approximately 6%. The cell system was then dismantled and the apparatus prepared for a set of similar experiments at a higher calcium oxide concentration.

Calculations

The procedure in purifying the components, in measuring the amount of each and in determining the vapor pressures and conductivities was long. A large number of calculations were required, as extreme care had to be exercised to make all the necessary corrections. An explanation of the different calculations is necessary.

The calcium oxide and water were weighed directly and, in addition to the buoyancy correction, it was necessary to correct for the amount of water vapor remaining in the distillation bulb after it had been sealed from the reaction cell. In calculating the weight of sulphur dioxide introduced into the reaction cell, the molecular-weight—pressure relation of Cooper and Maass (3) was used. The height of mercury in the manometer was converted to that at 0° C. The pressure of the sulphur dioxide remaining in the tubing connecting the gas-measuring system to the reaction cell was that of the vapor pressure of sulphur dioxide at the temperature of a freezing mixture of carbon dioxide in acetone. Since the temperature and volume of the tubing were known, the weight of sulphur dioxide could be determined and corrections made. These amounted to less than 0.001 gm.

During an experiment there was always a known amount of sulphur dioxide in the vapor phase above the solution in the reaction cell. The volume of the vapor phase decreased with increase in temperature. This decrease could be calculated. The partial pressure of the sulphur dioxide could be determined for each temperature studied, and therefore the weight of sulphur dioxide in the vapor phase determined. The total weight of sulphur dioxide in the reaction cell was known, and therefore the weight in the liquid phase could be estimated.

In order to obtain accurate vapor pressure values, the following precautions were necessary. The scale with which the height of mercury was read was carefully calibrated. A series of thermometers hung along the manometer gave the temperature of both the mercury and the air above the mercury. Thus the necessary zero scale correction could be calculated. The volume of the manometer tubing was accurately known throughout its entire length, thus making it possible to determine the volume of enclosed air for any position of the mercury meniscus. Before an experiment, the manometer constant was carefully determined. This was necessary for calculating the pressure due to the enclosed air.

Before conductivity determinations could be made, the cell constant was evaluated by means of $N/10$ and $N/50$ potassium chloride. The lead resistance was determined by filling the cell with mercury and balancing the resistance against that of a standard. Specific conductivities were calculated in the usual manner.

From the foregoing it will be seen that the corrections necessary to give true concentrations in the liquid phase could be made. Special care was taken in determining the weight of sulphur dioxide added. The accuracy was 1 in 10,000, so that after six additions the concentration was known to better than 1 in 1000.

Results

Approximately 24 concentrations were studied and for each of these a series of readings was made at eight different temperatures. Before all the data could be correlated and condensed into Tables I and II, several hundred curves had to be drawn.

On account of the space that would be required, it is impossible to include the data and graphs from which the tables of vapor pressures and conductivities were derived. The method used, however, is as follows. Starting with one concentration of calcium oxide and sulphur dioxide, a set of vapor pressures and conductivity values was obtained in the temperature range 25° to 130° C. As the procedure in determining the vapor pressures and conductivities was the same, only the former will be described. Vapor pressures were plotted against temperatures. A second experiment was performed using the same amount of calcium oxide but a higher sulphur dioxide concentration. Thus a second curve was obtained in which the vapor pressures were higher. In this manner a series of curves was obtained for a number of experiments in which the calcium oxide concentration was constant, but the sulphur dioxide concentration differed for each experiment. From the series of curves a set of isotherms at 25°, 50°, 70°, 90°, 110° and 130° C. was drawn in which vapor pressures were plotted against percentage sulphur dioxide.

The foregoing procedure was applied to each of the four calcium oxide concentrations studied. The next step involved the correlation of these data, together with the addition of the data of Campbell and Maass (1). For one temperature (*i.e.*, 25° C.) and one sulphur dioxide concentration (*i.e.*, 1%), vapor pressures were plotted against per cent calcium oxide. The necessary values were taken from the five series of graphs described above. A curve was then plotted from the data obtained at a temperature of 25° C. and with a sulphur dioxide concentration of 2%. Similar curves were drawn for concentrations of sulphur dioxide of 3, 4, 5 and 6%. This completed the data for the temperature 25° C. Similar sets of curves were drawn for temperatures of 50°, 70°, 90°, 110° and 130° C. The results shown below were obtained from this final group of curves.

Table I contains the vapor pressure values over the concentration and temperature ranges stated above. The conductivity values contained in Table II include the same concentration range, but no values are given for temperatures higher than 90° C. There are two reasons for this: (i) Campbell's data for 0% concentration were not complete at temperatures higher than 90° C.; (ii) in the higher temperature range, precipitation of calcium sulphite takes place, and this is accompanied by a sudden change in the direction of the conductivity curve, making interpolation difficult.

The data in Tables I and II provide a wide field for theoretical consideration. The most interesting study is that of the various equilibria existing in the system calcium-oxide–sulphur-dioxide–water. It is the intention of the authors to evaluate the various ionic concentrations. In a later paper a method of arriving at the hydrogen ion concentration will be presented.

TABLE I

Vapor pressures of the system calcium-oxide–sulphur-dioxide–water

SO_2, %	CaO, %	Temperature, °C.					
		25	50	70	90	110	130
		Vapor pressure, cm.					
1	0 0	8.7	25.8	52.3	95.8	166.0	275
1	0.5	6.3	17.2	40.4	71.5	129.5	235
1	1.0	3.8	11.9	29.4	57.2	115.0	212
1	1.5	2.7	9.2	22.0	52.2	108.4	203
1	2.0	2.5	9.0	22 0	52.0	107.0	202
1	2.5	2.5	8.8	22.0	51.6	107.0	202
2	0.0	17.1	43.9	82.5	142.3	231.0	353
2	0.5	11.4	29.8	62.1	100.8	179.4	303
2	1.0	7.5	19.1	41.7	75.7	146.5	263
2	1.5	5.3	12.5	25.4	63.0	125.4	240
2	2.0	3.0	9.0	22.0	56.2	116.4	220
2	2.5	2.5	9.0	22.0	52.4	107.6	210
3	0.0	26.0	63.8	104.5	190.0	292.5	431
3	0.5	18.8	47.0	87.8	140 0	234.1	375
3	1.0	12.3	41.6	61.5	106.4	193.0	325
3	1.5	8.5	20.3	43.2	86.8	162.0	295
3	2.0	6.2	13.2	35.1	74.3	139.8	275
3	2.5	3.7	11.1	31.0	66.4	127.4	256
4	0.0	36 4	85.2	148.0	236.5	356	518
4	0.5	29.5	68.2	118.8	189.8	295	462
4	1.0	23.3	51.9	91.0	151.8	250.5	409
4	1.5	17.0	36.4	67.2	123.4	217.6	372
4	2.0	11.2	22.0	53.2	102.2	190.0	340
4	2.5	5.8	13.2	46.0	88.1	169.8	314
5	0.0	46.4	106.7	180.3	282.7	420	610
5	0.5	41.5	91.6	155.5	244.5	374	560
5	1.0	35.5	75.6	130.4	210.3	332	516
5	1.5	29.0	57.2	105.4	180.0	293	467
5	2.0	18.1	36.6	80.3	152.0	256	420
5	2.5	8.4	18.3	62.6	130.5	226	377
6	0.0	56.8	127.6	223.4	329.6	484	709
6	0.5	54.1	117.3	198.4	302.1	452	675
6	1.0	49.4	102.4	175.5	275.0	414	635
6	1.5	42.0	79.2	140.1	242.4	375	580
6	2.0	27.4	55.4	110.0	210.5	331	516
6	2.5	12.5	32.5	85.8	179.6	290	450

TABLE II

CONDUCTIVITIES OF THE SYSTEM CALCIUM-OXIDE-SULPHUR-DIOXIDE-WATER

SO_2, %	CaO, %	Temperature, °C. 25	50	70	90
		Specific conductivity, ohms^{-1}			
1	0.0	0.0190	0.0188	0.0175	0.0150
1	0.5	.0150	.0137	.0150	.0128
1	1.0	.0090	.0057	.0061	.0054
1	1.5	.0065	.0070	.0070	.0090
1	2.0	.0065	.0075	0082	.0095
1	2.5	.0065	.0075	.0082	.0095
2	0.0	.0265	.0254	.0240	.0208
2	0.5	.0237	.0264	.0304	.0351
2	1.0	.0180	.0260	.0329	.0390
2	1.5	.0118	.0216	.0278	.0346
2	2.0	.0055	.0093	.0108	.0126
2	2.5	—	—	—	—
3	0.0	.0330	.0327	.0286	.0245
3	0.5	.0272	.0335	.0370	.0421
3	1.0	.0239	.0330	.0423	.0500
3	1 5	.0212	.0300	.0410	0477
3	2.0	.0195	.0235	.0300	.0321
3	2.5	.0180	.0157	—	—
4	0.0	.0383	.0376	.0330	.0280
4	0.5	.0313	.0380	.0406	.0443
4	1.0	.0277	.0380	.0456	.0530
4	1.5	.0265	.0377	.0351	.0523
4	2.0	.0267	.0367	.0418	.0455
4	2.5	0284	.0354	.0327	.0316
5	0.0	0435	.0415	.0370	.0310
5	0.5	.0348	.0398	.0423	.0450
5	1.0	.0317	.0400	.0468	.0535
5	1 5	.0321	.0420	.0500	.0553
5	2 0	.0342	.0457	.0520	.0532
5	2.5	.0375	.0510	.0535	.0497
6	0 0	.0475	.0455	.0400	.0335
6	0.5	.0372	.0415	.0432	.0455
6	1 0	.0342	.0412	.0474	.0535
6	1.5	.0352	.0452	.0528	.0575
6	2.0	.0381	.0530	.0598	.0588
6	2.5	.0424	.0635	.0677	.0593

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AN X-RAY METHOD FOR THE STUDY OF "BOUND WATER" IN HYDROPHILIC COLLOIDS AT LOW TEMPERATURES[1]

BY W. H. BARNES[2] AND W. F. HAMPTON[3]

Abstract

A new method for the study of hydrophilic colloids by the application of X-ray methods of analysis to the frozen gels is described. The possibilities of the method and its limitations are shown by a qualitative study of the amount, and variation with temperature, of the so-called "bound" water in gelatin gels over the temperature range −3° to −50° C.

Introduction

The quantitative estimation of the relation between the amount of unfrozen, or so-called "bound", water and temperature in systems of hydrophilic colloids in general, and gelatin in particular, has been the subject of a number of investigations. The most important procedures adopted for this purpose have been calorimetric, dilatometric, and analysis of the core of frozen specimens. The historical development of these methods has been reviewed by Jones and Gortner (12). In the first two of these methods the amount of "bound" water is determined as the difference between the total quantity of water in the system and the experimentally measured quantity of "free" water; in the third it is obtained by direct analysis. "Bound" water obviously is defined by these procedures as the water that will not freeze at temperatures below 0° C.—a definition that is adhered to in the present paper.

The necessity for caution in the interpretation of the results obtained with the calorimetric method has been pointed out recently on theoretical and experimental grounds (7, 8). It appears that total heat measurements of gelatin gels are complicated by the fact that not only may the relative amount of "bound" water vary with the temperature, but the relative intensity of the forces involved in the "binding" probably is not constant over a temperature range. Any such variation in the amount of "bound" water or in the intensity of "binding" might well be associated with a heat effect of unknown magnitude (11).

The dilatometric method is comparatively simple, involves no complex calculations, and is readily adaptable to almost any kind of material. Furthermore, it possesses the obvious advantage of being applicable to the study of the amount of frozen ("free") water at different temperatures, without involving a change in the temperature of the sample during the time of each observation at a given temperature. It has, however, been pointed out to the writers by Dr. J. H. Mennie that there is a similar need for caution in considering the results obtained with this method. If the amount of "bound" water or the intensity of "binding" varies with temperature, an uncertain variation in the specific volume of the "bound" portion of the water may be introduced.

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Moran (14, 15, 16) has found that with slow freezing the "free" water separates as ice entirely on the surface of the gel. The relative amount of "bound" water, therefore, may be obtained by an analysis of the concentration of the core of the frozen specimen. He has employed this method for the estimation of the relative amounts of "bound" water in frozen gelatin gels over a temperature range, and for the study of the effects of different rates of freezing. It is the most direct of the three methods.

The results obtained by Jones and Gortner (12) with a dilatometer indicate that the amount of "bound" water in gelatin gels is independent of temperature between about −6° and −50° C., if sufficient time is allowed for equilibrium to be established at the higher temperature, but varies with gel concentration. Moran found that the amount of "bound" water apparently is independent of temperature below −19° C., and does not vary with gel concentration, at least between the limits of about 12 to 44%. According to Briggs (5) the amount of "bound" water should depend on temperature but not on gel concentration.

In view of these conflicting data it seemed desirable to develop an independent method for the study of the amount of "bound" water in frozen hydrophilic colloids, and particularly in gelatin gels, at different temperatures. The investigation reported in this paper was undertaken with a view to examining the possibility of the application of the methods of X-ray analysis to this end. A large number of X-ray diffraction studies have been made of unstretched gelatin gels at ordinary temperatures, but apparently no previous attempt has been made to apply them to frozen gels.

Briefly the procedure described in this paper consists in taking series of X-ray photographs of frozen gelatin gels of different concentrations at known temperatures by the monochromatic pin-hole method. The presence or absence in the resulting diagrams of diffraction effects due to ice shows the presence or absence of "free" (frozen) water in the gel samples. The relative amount of "bound" water at any given temperature is then obtained from the known concentration of the most dilute gel whose X-ray diagram shows no evidence of the presence of ice, and from the known concentration of the most concentrated gel whose X-ray diagram does show the presence of ice.

Experimental

X-ray Equipment

The X-ray tube was of the Shearer type equipped with a copper target ($\lambda_{K\alpha} = 1.54$ Å) and a window of nickel foil to remove the K_β radiation. It was operated at about 45 to 50 kv. and 5 to 6 ma. from a Watson transformer.

For preliminary photographs of gelatin gels at a single low temperature (3, 6), the sample was placed on top of a cylindrical lead block pierced vertically with a 1 mm. pin hole for definition of the X-ray beam. The lead block was packed in solid carbon dioxide during exposure of the sample to X-rays. The flat photographic film was supported above the sample and perpendicular to the X-ray beam on a brass cylinder whose axis coincided with that of the pin hole. Tests with a thermocouple showed that by this means a very steady temperature of about −50° C. was obtained at the gelatin sample.

In order to study the effect of temperature, a new X-ray camera was designed (2). It is described in detail elsewhere (4). It is applicable to the examination of a large variety of materials when a single crystal spectrograph is not required, and may be employed for photographs over a large temperature range.

The essential features of this camera are as follows. The sample is held in position on a circular copper block around the circumference of which is soldered a copper tube through which a suitable liquid at any desired temperature may be circulated. The X-ray beam, defined by pin holes of any desired diameter, passes normally through a small hole in the copper block and thus through a small portion of the sample under investigation. The X-ray film or plate is held normal to the beam in a specially designed plate holder, and suitable means are provided for obtaining various crystal-to-plate distances. The whole camera is vapor tight. For the present experiments the copper block, and hence the sample, was cooled by circulating acetone at adjustable low temperatures through the copper tube. The temperature of the sample was determined by means of a copper-constantan thermocouple, which was calibrated against a standard thermometer over the range 0° to −40° C., and at the sublimation point of carbon dioxide (−78 5° C.). The temperature of the sample as shown by the thermocouple was kept constant during an exposure by adjusting the temperature of the acetone in the circulating system. Eastman Dupli-Tized X-ray films were employed throughout this investigation, and it was found to be of definite advantage to back them with a Patterson intensifying screen.

Gelatin

Eastman "ash-free", isoelectric gelatin (lot No. 48) was employed for all the present determinations. It was dried by storing small strips over phosphorus pentoxide in a desiccator under vacuum for a period of seven months before use. During the subsequent period of about six months during which the X-ray photographs were taken, the strips were kept in the same desiccator and under the same conditions. As a control one of the strips was weighed periodically during this latter time and no loss in weight was observed. As a further check on the dryness of the samples two of them were heated for 48 hr. to constant weight in a drying oven at 105° C. A negligible loss in weight, corresponding to less than 0.005 gm. of water per gm. dry gelatin, occurred.

Gels of different concentrations were prepared as follows. A weighed strip of dry gelatin was immersed in distilled water until the approximate concentration desired was obtained. Surface water was removed by blotting the strip between pieces of clean filter paper and then waving the gel back and forth in the air for a few seconds. The sample was then weighed again and the amount of water per gram of dry gelatin was calculated.

The gel was placed in position on the cooling block of the X-ray camera as rapidly as possible in order to minimize change of concentration due to evaporation of water. The camera was closed with the previously loaded plate holder, and the temperature of the sample was reduced rapidly to about −60° C. and kept at that point for five or ten minutes. The temperature of the gel was then raised slowly to that desired. When this became constant the X-ray tube was brought into operation. Exposures of about one hour to the X-ray beam gave satisfactory photographs.

The procedure of first freezing the gels rapidly at a low temperature was adopted primarily because it was desired to obtain as uniform a deposition as possible of small ice crystals throughout the samples in the case of gels containing "free" water, rather than the separation of ice only on the surface as reported by Moran (14) for slow rates of freezing.

At the end of the exposure to the X-radiation the gel was removed as rapidly as possible and reweighed. This was found to be necessary because a loss in weight of about 3% always occurred between the time at which the sample was weighed just before the exposure and the time afterwards. All weighings were made with the specimen in a small tightly stoppered weighing bottle.

Repeating the procedure outlined above, but with the gel in the camera for only about five minutes, showed that, at least for the exposure times employed in these experiments, virtually all the loss in weight took place during the transfer of the gel, and virtually none during the time of exposure of the frozen gel to X-rays. Since the time elapsing from the weighing of the gel to the beginning of the exposure, and that from the end of the exposure to the final weighing, were approximately the same, the concentration of the frozen gel was taken as the mean between the values before and after the exposure.

Detection of Ice

Since the method described in this paper depends on the detection of ice by means of X-rays, it was necessary to determine approximately how small a quantity of free ice would yield a recognizable diffraction pattern in the presence of dry gelatin during a reasonably short exposure to the X-ray beam.

For this purpose X-ray photographs were taken of measured quantities of ice deposited from the vapor state uniformly over the surfaces of thin strips of magnesium foil. The weights of ice in the path of the beam were calculated from the total weights of the deposits and the areas of the magnesium strips. From the average dimensions of the gel samples employed and the dimensions of the X-ray beam through the gels, these weights of ice were converted into the equivalents of grams of water per gram of dry gelatin. It was found that a quantity of free ice in the path of the beam corresponding to 0.01 gm. of water per gm. of dry gelatin could readily be identified. This was considered to be a small enough amount for the present investigation, so that it was unnecessary to determine the minimum quantity that could be detected. The presence of a strip of dry gelatin on top of the ice deposit, and hence between the ice and the photographic film, during the exposure did not interfere with the identification of this small amount of ice.

The detection of diffraction effects due to ice in photographs of frozen gels of concentrations close to the limits of maximum amounts of "bound" water, proved to be more difficult as the following considerations will indicate.

The principal features of the complete X-ray diffraction pattern of unstretched gelatin (10) consist of more or less sharply defined rings at 2θ angles* of about 4°, 8°, and 32°, respectively, and "amorphous" haloes at about 12°, 20°, and 42°, respectively. Of these, the rings at 4° and 8° were not observable in the present study owing to the short crystal-to-plate distances employed, and the halo at 12° (reported to appear on the plates only after very long exposures (10)) was not visible after the comparatively short exposure times adopted in the present investigation. Identification of gelatin, therefore, was limited to the haloes at about 20° and 42°, and to the ring at about 32°.

Of the complete powder pattern due to randomly distributed small crystals of ice (1), rings with 2θ angles greater than about 45° either were outside the range of the plate holder or required unduly long exposure times for their appearance on the photographic films. Identification of ice, therefore, was confined to the diffraction rings at 2θ angles less than this, namely, at 22°36′, 24°0′, 25°38′, 33°12′, 39°42′, and 42°12′, respectively. Of these, the first three were not resolved at the crystal-to-plate distances (2.23 to 3.67 cm.) employed and with a 1 mm. pin hole, so that they appeared on the photographs as a single diffraction band at an average 2θ angle of about 24°.

Essentially, therefore, the identification of ice in the presence of dry gelatin consisted in observing the superimposition of a set of ice rings at 24°, 33°12′, 39°42′, and 43°12′ on the pattern for dry gelatin at 19°16′ (13), 31°56′ (13), and 41°53′ (10). This was readily accomplished by simple visual inspection of the photographs.

In the case of frozen gelatin gels, however, conditions are complicated by the fact that the positions of the haloes and rings due to dry gelatin vary with decreasing concentration of the gel. For example, when dry gelatin is allowed to swell in water vapor at room temperature, Katz and Derksen (13) have found that the 2θ angle of the halo at 19°16′ increases to 26°16′, while that of the ring at 31°56′ decreases to 30°42′, as the dilution increases to 266 parts of water per 100 parts of dry gelatin. In passing it may be noted that although they report the absence of the ring at 31°56′ in dry gelatin, it appears in all the photographs of dry gelatin obtained during the present investigation, although of very weak intensity.

Reviewing the foregoing data, it will be seen that the gelatin halo at 41°53′ lies between the ice rings at 39°42′ and 43°12′. It was found that this halo overlapped the pair of ice rings in the photographs, and made their presence indiscernible when only very small quantities of ice were present. Attempts were made to measure the intensities of these ice rings in more dilute gels with a Moll microphotometer, in the hope that a curve of the intensities of these lines plotted against gel concentrations could be extrapolated to zero intensity and thus enable the concentration of the gel at which these lines disappeared to be determined. This proved to be impossible, however, because of the pronounced background fogging on the films.

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*In this paper diffraction rings and haloes are designated in terms of their 2θ angles, where 2θ is the angle between the incident and diffracted X-ray beams, i.e., twice the angle of diffraction, θ, in the Bragg equation, $\lambda = 2d \sin \theta$, for $\lambda = 1.54$ Å

Turning now to the gelatin ring at 31°56′, it is evident that no clear separation of this ring from the ice ring at 33°12′ could be expected, except for very dilute gels or for longer crystal-to-plate distances or smaller pin holes than were employed in the present experiments.

There remains, therefore, only the ice band at 24° and the gelatin halo at 19°16′. The variation of the latter with gel concentration at room temperature is shown in Fig. 1, where the circles represent points calculated from the data of Katz and Derksen (13) and the crosses represent values obtained for similar gels at room temperature during the present investigation, in order to compare the accuracy of the present measurements with the apparently very careful work of Katz and Derksen. The heavy horizontal line shows the position of the ice band at 24°. From the curve it will be seen that a reasonable separation of the gel halo and ice band occurs in the more concentrated gels, at least from 0 to about 0.55 gm. of water per gm. of dry gelatin.

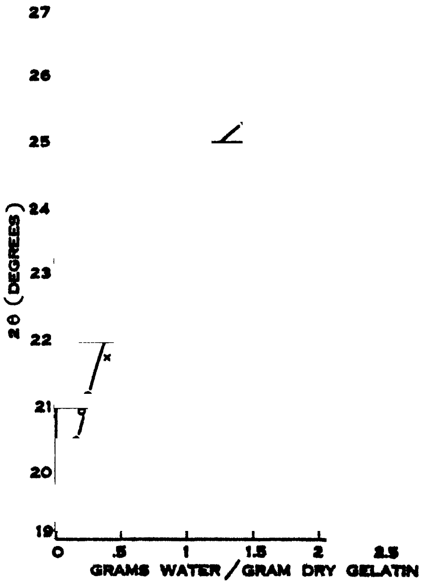

FIG. 1. *Variation of 2θ with concentration at room temperature.*

For the results reported in the next section, therefore, attention was centered on this gelatin halo and the ice band.

Results

The results obtained are summarized in Table I, in which the temperature for each set of observations is shown in brackets. Columns 1 and 5 give the concentrations of the gels in terms of grams of water per gram of dry gelatin; Columns 2 and 6, the observed 2θ angle of the halo or band in the region of 19° to 24°; Columns 3 and 7 the 2θ value, obtained from Fig. 1, for the corresponding gelatin gel halo at room temperature. In Columns 4 and 8 the presence or absence of randomly distributed diffraction spots on the photographs due to ice crystals in the samples is indicated by the letters *P* and *A*, respectively.

TABLE I

VARIATION OF 2θ WITH CONCENTRATION AT VARIOUS TEMPERATURES

Concentration	2θ angles		Comments	Concentration	2θ angles		Comments
	Obsd.	From Fig. 1			Obsd.	From Fig. 1	
(−53.2° C.)				(−25.4° C.)			
0.36	20°52′	21°57′	A	0.42	22°32′	22°18′	A
0.41	20°52′	22°16′	A	0.45	23°37′	22°30′	P
0.42	21°58′	22°18′	A	0.51	23°31′	22°51′	P
0.43	20°45′	22°27′	A				
0.45	23°43′	22°31′	?	(−11.5° C.)			
>0.8	23°56′	—	P	0.40	21°25′	22°15′	A
				0.45	22°19′	22°30′	A
(−39.8° C.)				0.51	22°32′	22°51′	A
0.34	21°58′	21°48′	A	0.55	23°4′	23°3′	?
0.41	22°32′	22°16′	A	0.59	23°4′	23°15′	P
0.42	22°44′	22°18′	A				
0.43	22°44′	22°27′	A	(−3.4° C.)			
0.46	23°56′	22°36′	P	0.42	21°25′	22°18′	A
0.47	23°56′	22°39′	P	0.47	22°32′	22°39′	A
				0.61	23°37′	23°18′	?

Examination of Table I shows that the observed 2θ angles for the more concentrated gels agree very closely with those at room temperature. At −53.2° C., −39.8° C., and −25.4° C., however, as the concentration decreases there occurs a small but sudden increase in the size of the halo to a value greater than that at room temperature, but approximately equal to that of the ice band, *i.e.*, about 24°. This increase in the size of the halo usually is accompanied by the appearance of randomly distributed diffraction spots on the photographs. It may also be noted that only one halo appears even in the more dilute gels. There is no visual evidence on the photographs of a broadening of the gel halo due to the superimposition of the ice band on its outer edge. In the photographs of the more concentrated gels the halo appears in approximately the same positions as at room temperature, in the photographs of the more dilute gels it appears in the approximate position of the ice band.

In Table I the 2θ values for the haloes due to the more concentrated gels at −53.2° C. do not agree as closely with those at room temperature as do those at the other temperatures. It will be seen, however, that in all cases they are smaller. This serves to emphasize the sudden increase in the 2θ angle between concentrations of 0.43 and 0.45.

Discussion

Since this investigation was concerned primarily with the general question of the applicability of X-ray methods of analysis to frozen gelatin gels, no attempt was made to determine with a high degree of accuracy the relative amounts of "bound" water at different temperatures. The numerical results obtained, therefore, are to be considered only as qualitative.

From the combined observations of the sudden increase in the diameter of the halo and the appearance of randomly distributed diffraction spots due to ice, the results indicate that the amount of "bound" water in gelatin gels is independent of temperature, at least between about −25° C. and −50°C. and corresponds to about 0.44 gm. of water per gm. of dry gelatin.

Above some temperature between −11° C. and −25° C., however, the amount of "bound" water apparently does vary with the temperature, because no increase in the "normal" diameter of the gelatin halo was observed at concentrations of 0.45 and 0.47 for temperatures of −11.5° and −3.4° C., respectively. In fact no sudden increase in the size of the haloes at these temperatures was observed even with concentrations as high as about 0.6. It follows, therefore, that at these temperatures the amount of "bound" water must be appreciably greater than that at the lower temperatures.

Reference to Fig. 1 shows that at a gel concentration of about 0.8, the ice band coincides in position with the galatin halo, and between 0.55 and 0.8 the maximum difference between the 2θ angles is less than 1°. From the change in position of the halo alone, therefore, it is not possible to recognize the first appearance of ice in gelatin gels of concentrations between about 0 55 and 0.8 without the use of longer crystal-to-plate distances or radiation of longer wave-length. Some evidence, however, is supplied by the presence or absence of the randomly distributed diffraction spots on the photographs. Thus at −11.5° C. no spots were observed for concentrations below 0.51, only two or three of questionable validity at 0.55, but unmistakable ones appeared in photographs of gels of concentrations about 0.59. At −3.4° C. no evidence of ice spots was obtained at or below a concentration of 0.47, while they were of questionable occurrence even in gels containing 0.61 gm. of water per gm. of dry gelatin.

These results, therefore, are in qualitative agreement with those of Moran (14) referred to above. Moran found that the amount of "bound" water in gelatin gels decreases with temperature from 0° C. to about −19° C., below which it remains constant at about 0.53 gm. of water per gm. of dry gelatin. At −3° C., for example, his data show an amount of "bound" water corresponding to about 0.84 gm. of water per gm. of dry gelatin. The results of the present study indicate that the amount of "bound" water at −3.4° C. probably is at least greater than 0.61, that at −11.5° C. it is about 0.55, and that it attains a value of about 0.44 at some temperature between −11.5° and −25.4° C. and then remains constant at least to about −50° C.

These results suggest, however, that Moran's value of 0.53 for the lower temperatures may be too high. This is supported by the fact that unmistakable ice spots were observed in the photographs of gels containing as little as 0.45 gm. of water per gm. of dry gelatin. This apparent disagreement may be due, of course, to the difficulty, so frequently encountered with gelatin, of reproducing results even with samples of pure isoelectric material from different manufacturers or from different lots, or to the tacit assumption inherent in any investigation that the "dry" gelatin really contains a negligible amount of water. It is also possible that at the lower temperatures in Moran's method all the "free" water does not separate as ice on the *surface* of the specimens, although it seems unlikely that this would have been undetected, considering the care with which Moran has developed his method.

It should be noted that the present method tacitly assumes the essential validity of Moran's contention that "free" water separates as crystals of ice when gelatin gels are frozen. The results obtained favor this hypothesis rather than the ideas of Hardy (9) relative to the separation of solid solutions of gelatin and ice.

If the amount of "bound" water in gelatin gels varies with the concentration over the whole concentration range, then at any given low temperature some water should freeze at all concentrations. The results of the present investigation show that this does not occur. On the other hand, if all the water is "bound" until a limiting dilution is reached after which the amount of additional water which is "bound" varies with the concentration, the present method of examination would yield no useful information on this point, because a quantitative estimation from the photographs of the relative amounts of ice present in the frozen gels containing "free" water is impractical and probably impossible.

Qualitative though the present results on gelatin gels may appear, they show that the method of examining frozen gels by means of X-rays offers definite possibilities of a new and useful approach to the problem of "bound" water in hydrophilic colloids. The chief drawback to the method is the fact that it is dependent on the uncontrollable factor that the haloes or lines obtained at ordinary temperatures from the system under examination must be separable from the lines due to ice when the "free" water is frozen. It is possible, however, that this might be overcome by the use of a semi-cylindrical or cylindrical camera and longer exposures, so as to make the identification of ice dependent on lines at much larger 2θ angles. This would involve the prevention of sublimation of the ice from the sample during exposure, or preferably the use of a more powerful X-ray tube to diminish the necessary time of exposure.

In conclusion it should be noted that both the gelatin halo at about 22° and the ring at about 32° disappear from their normal positions when gelatin gels containing "free" water are frozen. As previously mentioned in the case of the halo, only one band and one ring are observed corresponding to the nearest ice band (24°) and ring (33°12′), respectively, and these have the same visual appearance as when obtained from ice alone. It is not clear, therefore, whether the gelatin halo and ring vanish, or are simply superimposed on the corresponding ice band and ring. It is also of interest to mention that the photographs of very dilute gels (less than about 50% gelatin) at the lower temperatures show some fibering of the ice rings. It would appear therefore that further X-ray studies of frozen gelatin gels may throw some light on the structure of gelatin.

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CONTRIBUTION À L'ÉTUDE DE LA POLYMÉRISATION

I. FORMATION, PROPRIÉTÉS ET CONSTITUTION DES POLYINDÈNES, EN PARTICULIER DU "TRIINDÈNE"[1]

PAR J. RISI[2] ET D. GAUVIN[3]

Résumé

Les méthodes de préparation du diindène non saturé et du "triindène" ont été améliorées. Le "triindène" n'est pas un corps homogène, mais un mélange de polymères inférieurs dont le P.M. moyen correspond à $(C_9H_8)_3$. Il est le deuxième terme de la série polymère-homologue des polyindènes, le premier étant le truxane (ou son isomère saturé), lequel se forme par simple transposition du diindène non saturé sous l'influence de la chaleur. La synthèse du "triindène" ne se fait pas suivant une réaction à étapes, mais bien à partir de trois molécules d'indène sans intervention du diindène non saturé.

Le "triindène" est de caractère saturé: il forme exclusivement des produits de substitution avec le brome, comme d'ailleurs tous les polyindènes; il ne réagit pas avec la benzaldéhyde, la *p*-diméthyl-amino-benzaldéhyde, le nitrite d'amyle, le chlorure de nitrosyle et ne subit aucune polymérisation. Les réfractions moléculaires de l'indène, du diindène non saturé et de quelques polyindènes ont été déterminées.

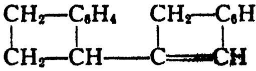
Les polyindènes résistent à l'oxydation par le permanganate de potassium et l'acide chromique. L'acide nitrique les oxyde à chaud en dérivés dinitrés et dicarboxylés sans rupture des molécules Les produits de dédoublement obtenus par distillation pyrolytique du "triindène" ont été caractérisés. L'essai de déhydrogénation catalytique du trimère n'a pas donné de résultat positif.

Les auteurs proposent une nouvelle formule filamentaire pour les polyindènes. Ceux-ci se formeraient par une réaction à chaîne, mais avec déplacement atomique (enchaînement condensant), donnant ainsi un produit intermédiaire avec double liaison. Par une réaction secondaire, les deux dernières unités du filament se cyclisent alors pour donner une molécule saturée avec boucle terminale. Les polystyrènes et les polyprènes devraient aussi avoir une constitution analogue.

Introduction

L'étude systématique des séries styrénique et indénique est très importante pour la connaissance des réactions de polymérisation en général. De nombreux travaux ont été faits surtout sur les polymères supérieurs des deux séries, tandis que les polymères inférieurs, à l'exception des dimères, ont été jusqu'ici peu étudiés. Leur connaissance pourrait sans doute apporter quelque éclaircissement dans la discussion du problème de la constitution des polymères. Nous avons entrepris dans ce but des recherches sur les polyindènes inférieurs, et plus spécialement sur le "triindène".

Les propriétés du diindène non saturé, préparé par Weger (28) et Weissgerber (29), ont été étudiées par Stobbe et Färber (20), par Whitby et Katz (30) et par Bergmann et Taubadel (2); les derniers auteurs ont établi définitivement sa constitution:



$$\begin{matrix} \mathrm{CH_2}-\mathrm{C_6H_4} & \mathrm{CH_2}-\mathrm{C_6H_4} \\ | \qquad\quad | & | \qquad\quad | \\ \mathrm{CH_2}-\mathrm{CH}- & -\mathrm{C}=\mathrm{CH} \end{matrix}$$

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[1] *Manuscrit reçu le 7 février, 1935.*

Contribution du département de chimie organique, École Supérieure de Chimie, Université Laval, Québec. Contribution basée sur une thèse présentée par Dominique Gauvin pour l'obtention du degré de D. Sc.

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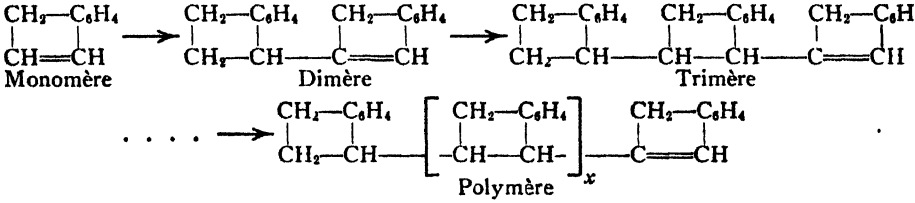
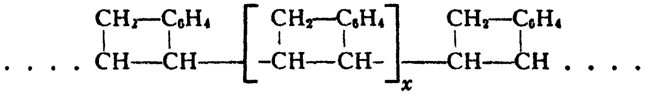
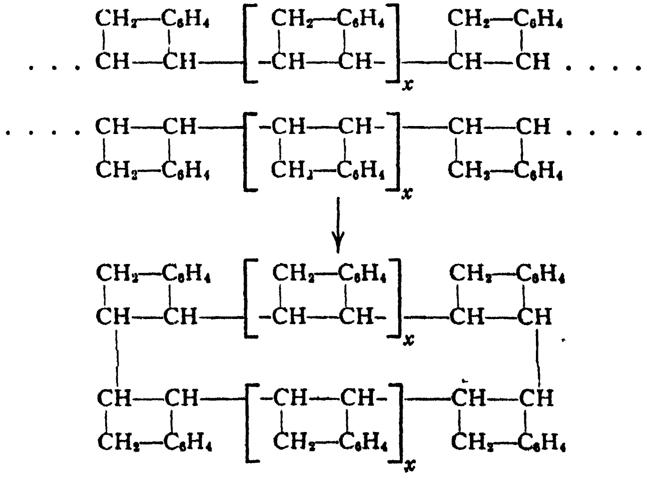
Whitby et Katz (30) ont été les premiers à obtenir un produit correspondant au triindène, soit par chauffage de quantités égales d'indène et de diindène non saturé, soit par dédoublement pyrolytique d'un polyindène supérieur. L'étude de l'absorption de brome les a conduit à la conclusion que ce nouvel "individu chimique", ainsi que les polyindènes pyrolytiques (30) et les polyindènes obtenus par action de la chaleur et des catalyseurs (31) sont des substances renfermant une double liaison par molécule. C'est cette observation qui appuie principalement la théorie des auteurs (31) sur la constitution et la formation des polyindènes, à savoir que ceux-ci sont formés par addition à étapes des molécules d'indène avec migration d'un hydrogène, suivant le schéma:



D'autre part, Staudinger (15) donnait d'abord aux polyindènes une formule à chaîne ouverte avec des valences terminales libres:

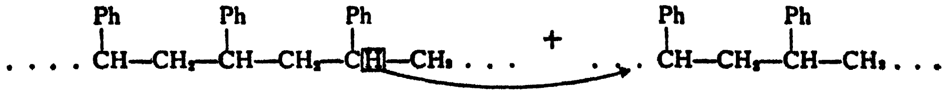


Plus récemment, Staudinger et ses collaborateurs (17) se sont exprimés plutôt en faveur d'une constitution cyclique, qui résulterait de la saturation des valences terminales libres d'une seule chaîne ou de deux chaînes parallèles préalablement formées. Le schéma pour le deuxième cas serait:



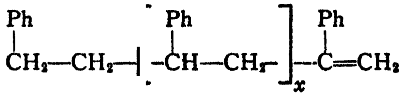
Cependant il a remarqué lui-même dans la suite (16, pp. 217 et 223) que l'existence de tels filaments doubles formant un anneau à P.M. élevé, à priori bien possible, est devenue douteuse à la suite de ses travaux sur la viscosité des acides polystyrène-carboniques.

Récemment, le même auteur (16, p. 223) a abandonné ses deux premières hypothèses, en assumant que, par une réaction secondaire, les filaments à valences terminales libres subissent une migration d'hydrogène, suivant le schéma:



$$\ldots\ \overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\overset{\displaystyle Ph}{\overset{|}{C}}\boxed{H}-CH_2\ \ldots \quad + \quad \ldots\ \overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2\ \ldots$$

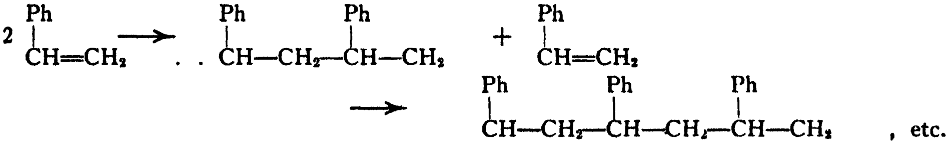
de sorte que chaque molécule du produit final possède une double liaison:



$$\overset{\displaystyle Ph}{\overset{|}{CH_2}}-CH_2-\left|\,-\overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\right]_x-\overset{\displaystyle Ph}{\overset{|}{C}}=CH_2$$

ce qui conduit à une formule analogue à celle préconisée par Whitby et Katz pour les polyindènes*. Il lui était cependant impossible de déceler avec certitude dans les polystyrènes des groupements finals non saturés ou autres.

Quant au mécanisme de polymérisation, Staudinger (16, pp. 149 et 223), ayant constaté que dans la polymérisation du styrène il se forme dès le début des produits à P.M. très élevé (16, p. 113) et que le di- et le tri-styrène n'additionnent pas d'autres molécules de styrène (16, pp. 149 et 222), admêt qu'une molécule de monomère soit activée par la lumière, l'oxygène ou des catalyseurs, et qu'une telle molécule activée peut ensuite s'unir à un grand nombre d'autres molécules sans déplacements atomiques, selon le schéma:



$$2\ \overset{\displaystyle Ph}{\overset{|}{CH}}=CH_2 \longrightarrow\ \ldots\ \overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2 \quad + \quad \overset{\displaystyle Ph}{\overset{|}{CH}}=CH_2$$

$$\longrightarrow \overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2-\overset{\displaystyle Ph}{\overset{|}{CH}}-CH_2 \quad \text{, etc.}$$

Chalmers (7) a calculé les constantes cinétiques d'un grand nombre de cas de polymérisation et a montré que celle-ci se poursuit à une vitesse quasi-unimoléculaire; il a conclu que le mécanisme de polymérisation ne peut être celui préconisé par Whitby et Katz, c.-à-d., addition par étapes: monomère + monomère = dimère; dimère + monomère = trimère, etc., mais qu'au contraire les polymères se forment directement par union de n molécules de monomère, suivant le schéma:

$$M \longrightarrow M \text{ (activé)} \qquad \text{Lentement}$$

$$M \text{ (activé)} + (n - 1)\, M \longrightarrow M_n \qquad \text{Instantanément}$$

Whitby et Katz, considérant que le problème de la constitution des polyindènes et du mécanisme de leur polymérisation peut difficilement être résolu par la seule étude des polymères supérieurs, ont été les premiers à attaquer la question par une étude systématique des termes inférieurs, pour lesquels il fallait même chercher une méthode de préparation convenable. Leur travail sur le triindène est sans doute à considérer comme un effort dans ce but. Sur la proposition des deux auteurs, nous avons continué cette étude, espérant pouvoir apporter quelque lumière dans ce problème si important et si complexe.

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* *Voir encore à ce sujet un travail de Staudinger et Steinhofer (Ann. 517 : 35-53. 1935), paru au cours de l'impression du présent travail.*

Partie Théorique

Préparation du diindène non saturé

La méthode de préparation du diindène non saturé de Stobbe et Färber (20) a été perfectionnée par Whitby et Katz (30). Par une modification légère, il nous a été possible de porter le rendement en diindène à 73% en maintenant 100 g. d'indène, 100 cc. d'acide chlorhydrique et 10 g. de pierre ponce à l'ébullition pendant 15 h. Les résultats des essais sont présentés dans le tableau I.

TABLEAU I

RENDEMENTS DANS LA PRÉPARATION DU DIINDÈNE NON SATURÉ

Temps de chauffage, h.	Acide chlorhydrique, %	Rendements en Indène, g.	Rendements en Diindène non sat., g.	Rendements en Polyindènes, g.
10	23	32	60	8
14	24	16	69	15
15	26	10	73	16

Préparation du "triindène" et preuve de sa non-homogénéité

La méthode de préparation du "triindène" donnée par Whitby et Katz (30) a d'abord été soumise à une étude systématique. Nous avons chauffé des quantités égales et équimoléculaires d'indène et de diindène non saturé en tube scellé à différentes températures pendant plusieurs jours. Les résultats sont donnés dans le tableau II, lequel contient les rendements en produits de distillation sur 10 g. de produits de départ. Un rendement maximum (56%) de la fraction de P.E. 215-240° C., contenant le "triindène", est obtenu par chauffage de quantités égales d'indène et de diindène à 215° C. pendant trois jours.

En remplaçant l'air dans les tubes par de l'azote, les rendements restent approximativement les mêmes.

TABLEAU II

PRÉPARATION DU "TRIINDÈNE" ET RENDEMENTS À PARTIR DE 10 g. DU MÉLANGE INDÈNE + DIINDÈNE NON SATURÉ

Produits de départ	Produits bruts de distillation	195°		215°		235°	
		5 jours	10 jours	3 jours	6 jours	3 jours	6 jours
Quantités égales	Indène g	1.0	0.7	1.0	3.5		
	Diindène, g.	3.3	3.0	2.5		3.9	3.8
	Fraction de P.E. 215-240°, g.	4.5	5.0	5.6	3.6	4.3	3.4
	Fraction de P.E. 240-275°, g.	0.8			1.7	1.5	1.0
	Résidu, g.		1.0	1.1	1.2		1.3
Quantités équimol.	Indène, g.	0.8	0.5	0.6	4.2		
	Diindène, g.	4.4	4.0	4.0			
	Fraction de P.E. 215-240°, g.	4.1	4.7	4.6	3.2		
	Fraction de P.E 240-275°, g.	0.4			1.3		
	Résidu, g.		0.7	0.7	1.1		

On obtient dans toutes ces préparations un produit secondaire, en proportions notables, qui cristallise du benzène en longues aiguilles du P.F. 214° C. Cette substance a pour formule brute $(C_9H_6)_3$ et possède un caractère saturé; son étude fera le sujet d'une autre communication.

Le "triindène" relativement le plus pur peut être obtenu de la fraction de P.E. 215-240° C. On y sépare d'abord la substance du P.F. 214° C. par un traitement à l'éther à froid, dans lequel elle est insoluble. La solution éthérée, après filtration, est évaporée à sec et le résidu est repris par l'alcool absolu à chaud; par refroidissement, il précipite un produit jaune pâle, de P.F. 70° C., correspondant au "triindène" décrit par Whitby et Katz (P.M. 357, 350) avec un rendement de 65% par rapport au produit brut. Par évaporation graduelle des eaux-mères, on peut récupérer plusieurs fractions inférieures de P.F. variant entre 50° et 60° C. et de P.M. entre 225 et 300 (rendement, 25-30%).

Le "triindène" du P.F. 70° C. est alors soumis soit à une précipitation fractionnée d'une solution éthérée par l'alcool absolu, soit à une dissolution fractionnée dans des quantités limitées d'alcool, dans le but d'étudier son degré d'homogénéité. Dans l'un et l'autre cas, l'on obtient à volonté un nombre de fractions de P.F. variant entre 63° et 90° C. et de P.M entre 310 et 425. La fraction correspondant le mieux au trimère, de P.F. 74° C. et de P.M. 370, est de nouveau fractionnée et elle montre encore un manque d'homogénéité. Il en est de même pour une fraction supérieure de P.F. 85° C., qui donne des sous-fractions d'un ordre dépassant légèrement le tétramère.

Il résulte ainsi la constatation importante que le produit considéré jusqu'ici comme triindène n'est pas un individu chimique homogène, mais que le "triindène" fait partie de la série des mélanges polymères, desquels il est impossible de séparer un individu uniforme, en d'autres termes, le "triindène" est un membre inférieur de la série polymère-homologue des polyindènes. Ceci est en accord avec une constatation analogue de Staudinger pour la série des polystyrènes et des polyindènes supérieurs (17, pp. 937 et 948; 19). Cette non-homogénéité du "triindène" explique aussi l'impossibilité de le cristalliser.

Un autre échantillon de "triindène", obtenu par dédoublement pyrolytique d'un polyindène supérieur d'après Whitby et Katz (30), est également non homogène et amorphe.

Mécanisme de formation du "triindène"

En admettant le mécanisme de formation proposé par Whitby et Katz (diindène + indène = triindène), le mélange idéal des produits réagissants devrait être équimoléculaire. Or, le tableau II montre qu'en opérant avec des quantités équimoléculaires d'indène et de diindène le rendement en "triindène" est inférieur à celui obtenu avec des quantités égales. On constate de plus que le pourcentage moyen de diindène récupéré est égal dans les deux cas, soit plus de 60% du diindène de départ. La perte d'environ 40% s'explique par la quantité notable de diindène récupéré par évaporation des eaux-mères de la fraction de P.E. 215-240° C., tel que déjà décrit, et surtout par la polymérisation individuelle du diindène (voir plus loin).

Ces observations nous ont conduit à l'idée que le diindène n'intervient pas du tout dans la synthèse du "triindène", et que par conséquent le mécanisme proposé par Whitby et Katz ne se réalise pas.

Afin de le confirmer de façon indubitable, nous avons chauffé de l'indène seul, du diindène seul, un mélange à parties égales d'indène et de diindène et finalement un mélange à parties égales d'indène et de kérosène pendant trois jours à 215° C. Les résultats sont donnés dans le tableau III.

TABLEAU III

CHAUFFAGE D'INDÈNE, DE DIINDÈNE NON SATURÉ ET DE KÉROSÈNE À 215° PENDANT TROIS JOURS

Produit de départ	Indène récupéré, g	Diindène récupéré, g.	Poly indènes, g	Fractionnement des polyindènes			
				Fraction	Quantité, g	P L	P M
I Indène, 10 g	0 7	—	9 3	1	4 5	108-110°	525
				2	0.9	83-85°	414
				3	1 0	75-77°	392
				4	0 6	62-65°	298
II Diindène non saturé 10 g	—	7 4	2 6	1	0 3	105°	440
				2	1 6	85°	352
III. Indène 10 g + diindène non saturé, 10 g	0 8	6 8	12 3	1	3 2	94-95°	459
				2	2 0	78-80°	356
				3	2 3	72-75°	344
				4	2 0	60-63°	292
IV. Indène 10 g + kérosène, 10 g	—	—	8 2	1	3 0	98-100°	502
				2	0 8	80-82°	400
				3	1 5	74-75°	378
				4	0 4	60-65°	293

Le tableau III montre que les quantités d'indène et de diindène récupérés et de polymères formés sont pratiquement les mêmes quand les deux réactifs sont chauffés séparément et en mélange. Nous avons là la preuve que l'indène et le diindène mélangés ne subissent qu'une polymérisation individuelle; car en admettant en plus une réaction mutuelle, la quantité de diindène récupéré devrait être beaucoup plus faible et le rendement en polymères plus élevé. Le fractionnement des polyindènes formés fait voir que, dans le cas du mélange indène-diindène, le degré de polymérisation est inférieur à celui atteint avec l'indène seul. Cet abaissement du degré de polymérisation est sans doute dû à la dilution et à la contrainte que subissent les molécules monomères au sein d'un liquide aussi visqueux que le diindène. En effet, déjà dans le cas d'un mélange indène-kérosène, où la mobilité moléculaire est moins restreinte, le degré de polymérisation est légèrement abaissé. Ces résultats sont d'ailleurs conformes aux observations de Staudinger (17, p. 934; 16, p. 158) et de Stobbe et Färber (20), qui ont constaté que le degré de polymérisation diminue graduellement avec la dilution des monomères.

Nous sommes ainsi en mesure d'affirmer expérimentalement les conclusions d'ordre mathématique de Chalmers (7) sur le mécanisme de polymérisation, c.-à-d., que le triindène est formé synthétiquement à partir de trois molécules d'indène et non par réaction d'addition de l'indène sur le diindène non saturé.

Transposition du diindène non saturé en diindène saturé

La preuve la plus sérieuse que le diindène non saturé (X) ne joue que le rôle d'un agent de dilution dans la synthèse du "triindène" est sa propre transposition en diindène saturé (truxane XI de Stobbe et Färber (20) ou son isomère VIII) au cours du chauffage. Aussi le "unchanged" diindène (non saturé), récupéré par Whitby et Katz (30, p. 360), n'est autre chose que du diindène saturé. A titre de comparaison, nous avons préparé du truxane par réduction de la truxone d'après Stobbe et Zschoch (24), et nous avons facilement constaté sa parfaite ressemblance avec notre diindène de récupération. Les deux ont les mêmes solubilités, le même P.E. (207° C. à 13 mm); ils sont saturés (voir plus loin: absorption de brome) et se conduisent de la même façon dans l'oxydation par l'acide nitrique, d. 1.25, à l'ébullition, tandis qu'ils résistent à l'oxydation par le permanganate de potassium et l'acide nitrique à froid. Afin de démontrer la transposition du diindène non saturé en diindène saturé encore plus nettement, nous avons chauffé le premier, seul, en tube scellé, à 215° C. pendant quatre jours, et l'absorption de brome (voir plus loin) prouve que sa transposition en diindène saturé est quantitative (abstraction faite de 40% de produit de départ qui se polymérise).

Cette constatation permet de dire que le diindène non saturé ne se range pas dans la série des polyindènes, vu qu'il ne se forme qu'en présence d'acides dilués comme catalyseurs et non par thermopolymérisation. A sa place nous devons mettre le diindène saturé qui est donc le premier terme de la série polymère homologue des polyindènes. Afin de bien distinguer dans la suite les deux isomères, nous appellerons celui considéré jusqu'ici comme diindène plutôt le 2-(α-hydrindyl)-indène.

Le fait que le P.F. du truxane cristallisé (116° C.) est supérieur au point de liquéfaction (P.L.) du "triindène" amorphe (72° C. environ) n'est pas un argument contre son incorporation dans la série des polyindènes, car un corps cristallisé a des constantes physiques beaucoup plus élevées que ce même corps associé à des polymères-homologues dans un mélange amorphe. Ainsi le dimère de l'α-méthyl-styrène cristallisé fond à 52° C., tandis que le même corps amorphe se ramollit et se liquéfie entre −32° et 24° C.; le tétramère cristallisé fond à 127-129° C., tandis qu'à l'état amorphe son point de liquéfaction est de 48° C. (18).

Ceci établi, nous avons entrepris l'étude comparative des propriétés des polyindènes, en particulier du "triindène".

Absorption de brome

Par bromuration d'un "triindène" de P.L. 70° C. avec un excès de brome en solution chloroformée à une température inférieure à 0° C., on obtient un produit bromé contenant un atome de brome par unité C_9H_8. La réaction se fait avec fort dégagement d'acide bromhydrique. En essayant une bromuration analogue avec une quantité de brome correspondante à deux atomes par molécule de "triindène", la réaction est incomplète, c.-à-d., il résulte un mélange du dérivé bromé précédemment mentionné et de l'hydrocarbure non attaqué.

Ces deux bromurations étant des substitutions, nous avons étudié comparativement le caractère de saturation de l'indène, du 2-(α-hydrindyl)-indène, du diindène transposé par chauffage et des polyindènes de différentes méthodes de préparation, en les soumettant à la bromuration d'après McIlhiney (12). Les résultats sont présentés dans le tableau IV.

Un essai en double opéré sur le "triindène" avec une solution de brome $N/10$ dans du chloroforme donnait des résultats semblables à ceux présentés dans le tableau pour le tétrachlorure de carbone comme solvant.

Le tableau IV permet de conclure que:

1. L'indène additionne exclusivement deux atomes de brome par mol.-g.

2. Le 2-(α-hydrindyl)-indène donne d'abord addition de deux atomes de brome par mol.-g., puis substitution allant jusqu'à un atome de brome lorsque l'excès de brome est suffisant.

3. Le truxane synthétique donne substitution exclusive, le degré de substitution augmentant avec la concentration de brome.

4. *a*. Le 2-(α-hydrindyl)-indène, après trois jours de chauffage à 185° C., est transposé à 40% en diindène saturé.

b. Cette transposition en diindène saturé de la partie non polymérisée est pratiquement quantitative en chauffant le 2-(α-hydrindyl)-indène pendant quatre jours à 215° C.

c Le diindène récupéré par distillation (fraction du P.E. 160° C. à 2 mm.) dans la synthèse du "triindène" (chauffage à 195° C. pendant trois jours) se compose de 58% de diindène saturé, le reste étant du 2-(α-hydrindyl)-indène.

5. Le "triindène" ne forme que des produits de substitution avec le brome. Avec une solution 0.08 N, l'équilibre de bromuration correspond à un dérivé monobromé, avec une solution $N/3$ à un dérivé dibromé et avec une solution normale à un dérivé tribromé.

6 et 7. Les polyindènes obtenus par polymérisation thermique de l'indène et par dédoublement pyrolytique des polyindènes ne donnent que substitution exclusive.

8 et 9. Les polyindènes catalytiques donnent substitution dont le degré augmente avec la température et la concentration de la solution bromée. De plus, le tableau montre apparemment une faible addition, mais nous croyons que les polyindènes catalytiques n'additionnent le brome pas plus que les autres. Les petites différences entre la quantité de brome consommée et substituée sont attribuables aux difficultés expérimentales, car le tétrachlorure de carbone n'est pas un bon solvant pour les polyindènes supérieurs;

TABLEAU IV

Bromurations d'après McIlhiney

Hydrocarbure	P.F. ou P.L., °C.	P M.	Poids de la substance, g.	Cc de CCl$_4$ comme solvant	Solution de brome dans CCl$_4$			Temp., °C.	Cc. de Na$_2$S$_2$O$_3$ N/10 correspondant au		Brome consommé		Br additionné, atomes par mol.-g.	Br substitué, atomes par mol.-g.
					0.08N cc.	N/3 cc.	N cc.		Br consommé	Br dégagé	Quantité moléculaire	Atomes par mol.-g		
1. Indène		116	0.5000	10		25		25	82.26	0.9	153	1.9	1.9	—
2. Diindène non saturé	P.F. 56	232	0.5064	10		25		5	48.90	5.05	179	2.24	1.8	0.44
		232	0.2483	25	50			25	20.55	—	154	1.9	1.9	—
		232	0.2264	25	50			25	19.70	—	161	2.0	2.0	—
		232	0.2766	10	50			25	25.3	1.1	169	2.1	1.95	0.1
		232	0.2373	10	50			25	22.1	1.7	172	2.15	1.9	0.1
		232	0.3045	10		25		25	51.71	14.36	315	3.9	1.8	1.05
		232	0.2925	10		25		25	34.15	5.0	216	2.7	1.9	0.4
3. Truxane synthétique		232	0.3040	10	50			25	11.7	6.0	72	0.9	—	0.45
		232	0.2381	10		25		25	18.6	9.4	145	1.8	—	0.9
4. Diindène chauffé (*a*)		232	0.2730	10	50			25	28.4	7.5	193	2.4	1.1	0.6
		232	0.2925	10		25		25	31.4	8.0	199	2.5	1.2	0.65
(*b*)		232	0.2381	10	50			25	18.2	8.9	142	1.75	—	0.85
		232	0.2231	10		25		25	25.5	12.45	212	2.65	—	1.3
(*c*)		232	0.2894	10	50			25	32.4	11.0	207	2.6	0.85	0.9
5. "Triindène"	P.L. 71–72	350	0.2715	25	50			25	18.66	10.17	190	2.3	—	1.15
		350	0.3027	25	50			25	21.21	11.10	194	2.4	—	1.2
		350	0.4000	10		25		25	48.31	24.04	338	4.2	—	2.1
		350	0.2593	10		25		25	29.17	15.00	312	3.9	—	1.95
		350	0.3863	10			25	25	70.76	39.85	509	6.3	—	3.15
6. Polyindène(*d*)	P.L. 102	451	0.6392	25	50			25	18.33	8.68	104	1.3	—	0.7
		451	0.4900	10		25		25	24.89	12.33	183	2.3	—	1.7
	P.L. 160	885	0.2324	10	50			25	6.2	3.3	188	2.35	—	1.2
		885	0.4329	10		25		25	16.1	8.4	263	3.3	—	1.65

TABLEAU IV—*Fin*

BROMURATIONS D APRÈS McILHINEY

Hydrocarbure	P F ou P L °C	P M	Poids de la substance g	Cc de CCl_4 comme solvant	Solution de brome dans CCl_4			Temp °C	Cc de $Na_2S_2O_3$ $N/10$ correspondant au		Brome consommé		Br additionné atomes par mol -g	Br substitué atomes par mol g
					0 08N cc	$N/3$ cc	N cc		Br consommé	Br degage	Quantité moleculaire	Atomes par mol g		
7 Polymdène(*e*)	P L 120	546	0 2509	10		25		25	20 00	10 95	347	4 3	—	2 15
8 Polyindène(*f*)	P L 185	1357	0 5026	10		25		5	14 75	7 15	318	3 97	0 03	1 97
		1357	0 5012	10		25		15	17 65	8 55	382	4 77	0 15	2 31
		1357	0 4996	10		25		25	18 00	8 95	390	4 87	0 03	2 42
		1357	0 4948	10		25		37	32 87	16 05	720	9 0	0 2	4 40
(*g*)	P I 220	2022	0 4994	10		25		5	8 7	3 85	281	3 51	0 4	1 55
		2022	0 5000	10		25		15	11 8	5 75	381	4 76	0 12	2 32
		2022	0 5006	10		25		25	12 4	5 85	400	5 0	0 28	2 36
		2022	0 5020	10		25		37	26 97	13 55	868	10 8	0 0	5 45
				Cc de $CHCl_3$ comme solvant	Solution de brome dans $CHCl_3$									
					0 08N	$N/3$								
9 Polyindène(*g*)	P L 220	2022	0 5020	25	50			25	6 6	3 4	212	2 65	0 0	1 33
	P L 210	1537	0 5052	25	50			25	7 2	3 4	175	2 18	0 12	1 03
	P L 180	1080	0 5010	25	50			25	10 0	4 5	172	2 16	0 22	0 97
	P L 220	2022	0 5100	10		25		15	11 9	5 7	377	4 71	0 2	2 25
		2022	0 5007	10		25		15	12 4	6 3	400	5 0	0 0	2 5
		2022	0 4938	10		25		37	29 8	14 75	975	12 2	0 2	6 0

(*a*) *Obtenu par chauffage du 2 (α hydrindyl) indène en tube scellé à 185° pendant trois jours* (*b*) *Obtenu par chauffage du 2 (α hydrindyl) indène en tube scellé à 215° pendant quatre jours* (*c*) *Récupéré dans la synthèse du triindène (chauffage à 195° pendant trois jours)* (*d*) *Polyindènes thermiques préparés d après Whitby et Katz (31)* (*e*) *Polyindène provenant de la décomposition pyrolytique d'un polyindène supérieur* (*f*) *Polyindènes catalytiques* (H_2SO_4) (*g*) *Polyindènes catalytiques* ($SbCl_5$)

nous avons toujours remarqué qu'une certaine proportion d'acide bromhydrique est énergiquement retenue par le tétrachlorure et qu'il faut une agitation très vigoureuse pour l'en détacher. Il s'agit très probablement d'un phénomène d'adsorption d'un électrolyte (acide bromhydrique) sur les particules semicolloïdales des polyindènes, cette adsorption demandant pour être rompue un meilleur contact avec les réactifs aqueux. C'est pourquoi nous avons aussi soumis des polyindènes catalytiques à la bromuration dans le chloroforme (groupe 9 du tableau), lequel est un meilleur solvant pour les polyindènes. En effet, la fin de la titration est plus facile à atteindre et l'addition apparente ne dépasse pas 0.2 atome par mol. Nous n'avons donc aucun doute sur le caractère saturé des polyindènes catalytiques, car une double liaison serait bien facile à déceler par la méthode de McIlhiney, même à basse température, comme l'indique le résultat obtenu avec le diindène non saturé à 5° C.

Autres preuves pour le caractère saturé des polyindènes

Ayant ainsi constaté le caractère saturé des polyindènes, nous avons voulu le confirmer davantage en les traitant par quelques réactifs spécifiques de la double liaison éthylénique. L'indène donne avec le chlorure de nitrosyle, suivant la méthode de Wallach et Otto (27), un nitroso-chlorure blanc et cristallisé, déjà vaguement mentionné par Dennstedt et Ahrens (8), qui fond à 148-150° C. avec décomposition. Il est instable et se transforme facilement par la chaleur en une substance huileuse brune. Le 2-(α-hydrindyl)-indène réagit également en donnant un nitrosochlorure instable, sous forme d'une huile verte passant au brun, qui donne toutes les réactions du nitrosochlorure, à savoir un précipité de chlorure d'argent avec une solution alcoolique de nitrate d'argent et mise en liberté d'iode avec une solution alcoolique d'iodure de potassium. Par contre, le "triindène" purifié le mieux possible se comporte dans les mêmes conditions comme corps saturé, car on le récupère quantitativement.

Si les polyindènes inférieurs étaient des corps non saturés, on devrait attendre l'existence dans la molécule d'un groupement CH_2 activé par le voisinage de la double liaison. Nous avons prouvé qu'un tel groupement CH_2 n'est pas présent, car un "triindène" débarrassé totalement du diindène non saturé ne réagit ni avec la benzaldéhyde, ni avec la *p*-diméthyl-amino-benzaldéhyde, et ne donne aucun dérivé nitroso avec le nitrite d'amyle, tandis que le diindène non saturé donne instantanément un nitroso-dérivé.

Si encore les polyindènes inférieurs étaient des corps non saturés, il faudrait sans doute leur attribuer une certaine aptitude à la polymérisation, quoique à un faible degré, puisque déjà le diindène non saturé se polymérise à un degré bien moins élevé que l'indène (30). Un "triindène" de P.L. 70° C. ne se polymérise aucunement ni par la chaleur, ni par l'acide sulfurique concentré. La chaleur cependant, selon la température et le temps de chauffage, transforme une partie du "triindène" employé en la substance de P.F. 214° C. déjà mentionnée et en truxène (tribenzylène-benzène), tel qu'il ressort du tableau V.

Un essai de polymérisation fait avec le pentachlorure d'antimoine sur le même "triindène" de P.L. 70° C. donnait d'abord un polymère correspondant à un hexamère, mais avec un si faible rendement que nous doutions que ce soi-disant hexamère provienne du trimère. En effet, en faisant réagir avec le pentachlorure d'antimoine un polyindène de P.L. 84-85° C. obtenu par fractionnement très soigné du "triindène" de P.L. 70° C., il ne se fait aucune polymérisation. Un autre essai sur un "triindène" préalablement débarrassé d'une trace de diindène non saturé par le nitrite d'amyle donnait aussi un résultat négatif.

TABLEAU V

ACTION DE LA CHALEUR SUR LE "TRIINDÈNE" (4 g.)

Température, ° C.	Temps de chauffage, jours	Produits		
		"Triindène" récupéré, g.	Substance de P.F. 214° C., g.	Truxène, g.
240	8	2 6 (P.L. 68° C.)	0 32	–
240	15	2 4 (P.L. 75° C.)	0 74	–
280	8	2 0 (P.L. 72° C.)	1 0	–
280	15	1 1 (P.L. 68° C.)	1 2	–
310	8	0 6 (P.L. 74° C.)	0 9	0 2
310	15	———	1 4	0 3

Nous avons aussi déterminé la réfraction moléculaire des polyindènes, ainsi que celle de l'indène et du diindène non saturé. Les résultats sont réunis dans le tableau VI.

TABLEAU VI

DENSITÉS ET RÉFRACTIONS MOLÉCULAIRES

Substance	Densité à 20° C.	Réfraction mol. calculée		Réfraction mol. trouvée
		Non-saturation	Saturation	
Indène	0 9991	37 75	36 04	38.31
Diindène non sat.	1 043	36 89	36 04	37 48
"Triindène", P.M. 350	1 082	36 61	36 04	36 58
Polyindène thermique, P.M. 447	1 083	36 47	36 04	36 27
Polyindène catalytique, P.M. 1146	1 099	36 21	36 04	35.90

Il serait sans doute difficile de tirer des conclusions certaines sur le degré de saturation du "triindène" et des polyindènes en se basant exclusivement sur la réfraction moléculaire, car les résultats obtenus ne paraissent pas suffisamment nets. Nous remarquons cependant que, tout en considérant une anomalie de l'indène semblable à celle du styrène, nos valeurs sont fort analogues à celles obtenues par Staudinger dans la série styrénique (16, p. 164).

Oxydation

Enfin, une dernière preuve pour l'absence d'une double liaison dans les polyindènes est fournie par l'oxydation. Le diindène saturé et tous les polyindènes ne sont pas attaqués par le permanganate en milieu acide et alcalin et par l'acide nitrique concentré à froid. Le "triindène" résiste aussi passablement bien à l'attaque par l'acide chromique, car on n'obtient qu'une très faible quantité d'un produit fondant à 120-123° C. et qui n'est pas de l'α-hydrindyl-hydrindone, à côté d'une trace d'acide phtalique, tandis que la majeure partie du produit de départ est récupérée. Le diindène non saturé par contre donne dans les mêmes conditions principalement de l'α-hydrindone (20).

En bouillant le 2-(α-hydrindyl)-indène pendant quatre heures avec de l'acide nitrique, d. 1.25, il y a oxydation complète; on obtient de l'acide phtalique comme produit principal, à côté d'une faible quantité (12%) d'un produit azoté de nature acide, P.F. 160-165° C. Le P.M. (390) montre que la molécule n'a pas été scindée et qu'au contraire il y a eu introduction de deux groupements NO_2 et probablement de deux COOH. N = 7.19%, correspondant à deux atomes d'azote par mol.-g.

Le diindène saturé fournit dans les mêmes conditions aussi de l'acide phtalique, à côté de 15% du même produit azoté décrit dans le cas précédent.

Tous les polyindènes thermiques et catalytiques, oxydés dans les mêmes conditions, donnent principalement un produit nitré analogue au précédent, à côté de peu d'acide phtalique. Les rendements en produit nitré augmentent graduellement avec le degré de polymérisation, alors que ceux de l'acide phtalique décroissent. Les P.M. des dérivés nitrés démontrent (voir tableau VII) qu'il n'y a pas eu rupture de la molécule, même dans le cas des polyindènes supérieurs. Tous ces produits d'oxydation sont constitués eux-mêmes par un mélange de dérivés nitrés-oxygénés de polymères-homologues, comme le démontre la précipitation fractionnée. Quoique l'interprétation

TABLEAU VII

PRODUITS D'OXYDATION DES POLYINDÈNES OBTENUS PAR ÉBULLITION AVEC L'ACIDE NITRIQUE, d 1.25, PENDANT TROIS À QUATRE HEURES

Produit de départ				Produit d'oxydation azoté										
											COOH		Nombre de	
Polyindène	P.L., ° C.	P.M.	g.	Rendement brut, g.	Fract.	P.L., ° C.	P.M.	C %	H %	N %	% Ag	% Cl	NO_2 (par mol.)	COOH (par mol.)
"Triindène"	72	364	5	4.5	1	210	594							
					2	225	667	61.67	3.82	3.55		7.91	1.75	1.5
thermique	115	562	5	5.6	1	240	761	62.97	3.86	3.46			1.9	
					2	260	850					6.83		1.7
catalytique (H_2SO_4)	142	712	5	6.3	1	245	850							
					2	260	1059					6.55		1.9
					3	270	1143	65.85	3.88	2.28	20.4		1.9	2.1
catalytique ($SbCl_5$)*	205	1387	3	3.8	2	280	2145							

des résultats analytiques soit plus difficile dans de tels cas, on peut tout de même constater l'entrée de deux NO_2 et deux COOH par molécule et d'un autre oxygène par unité C_9H_8. Les fonctions COOH ont été déterminées au moyen du chlorure de thionyle ou de leurs sels d'argent. Le tableau VII indique des détails plus précis sur ces résultats.

L'oxydation par le mélange nitrique-sulfurique est par contre plus énergique, car il y a rupture de la molécule en deux fragments et introduction d'un groupement NO_2 par unité C_9H_8. Ces produits d'oxydation sont également de nature acide et ont des propriétés semblables à ceux obtenus par l'acide nitrique seul, à l'exception cependant d'un caractère explosif assez marqué. Les rendements sont plus faibles, car l'oxydation plus énergique conduit probablement jusqu'à l'anhydride carbonique. Le tableau VIII résume les résultats obtenus.

TABLEAU VIII

PRODUITS D'OXYDATION DES POLYINDÈNES OBTENUS PAR ÉBULLITION AVEC UN MÉLANGE D'ACIDE NITRIQUE ET D'ACIDE SULPHURIQUE

Produit de départ					Produit d'oxydation					
Polyindène	P L, °C	P M	g	Temps de chauffage, h	Rendement brut, g	Fract	P L, °C	P M	N %	Nombre de NO_2 par mol.
Thermique	125	580	2	15	0 5	1	205	476		
Catalytique (H_2SO_4)	142	712	4	1	4 5	1	245	661	7 35	3 5
						2	225	590	7 51	3 2
Catalytique (H_2SO_4)	142	712	4	4	2 5	1	240	675		

Essai de déhydrogénation catalytique du "triindène"

Nous avons voulu établir une preuve directe pour la constitution du trimère de l'indène. Si ce corps était un dérivé du cyclohexane (voir plus loin), il devrait donner du truxène (tribenzylène-benzène) par déhydrogénation catalytique avec le palladium d'après Zélinski (32) et Tausz et Putnoky (25). Le résultat fut négatif, et il prouve plutôt que les polyindènes sont des substances filamentaires simples.

Dédoublement pyrolytique du "triindène"

Le dédoublement pyrolytique du "triindène" par chauffage à 335-340° C., pendant trois à quatre heures, fournit par distillation d'abord à pression ordinaire de l'indène (30-40%), puis sous pression réduite une huile visqueuse (10%) dont le point d'ébullition correspond au truxane et au 2-(α-hydrindyl)-indène et de laquelle nous n'avons pu isoler à l'état cristallin qu'une faible quantité du dernier (P.F. 55° C.), la majeure partie de cette fraction étant probablement du diindène saturé que nous tenterons d'identifier. Le résidu est formé par du "triindène" non attaqué (5%), la substance de P.F. 214° C. déjà mentionnée (20%) et du truxène (10%). Cette réaction est un "cracking" ordinaire qui peut s'appliquer tout aussi bien aux hydrocarbures aliphatiques que polyméthyléniques. Des dédoublements pyrolytiques analogues sont connus en assez grand nombre pour des corps cycliques, par exemple les acides truxiliques et truxiniques (21), le bis-cyclo-pentadiène (23) et surtout le truxane qui se dépolymérise en indène par chauffage (24). Le produit primaire du dédoublement pyrolytique du "triindène" paraît être de l'indène uniquement, lequel formerait en seconde phase par repolymérisation un peu de dimère et du truxène, selon le mécanisme exposé par Stobbe et Zschoch (24).

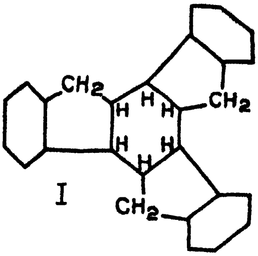
Constitution des polyindènes

Les deux premières formules proposées par Staudinger et ses collaborateurs (voir Introduction) doivent être définitivement abandonnées. Leur formule à valences résiduelles ne s'accorde pas avec l'absorption de brome et la résistance à l'oxydation; elle serait même tout-à-fait inconcevable pour les polymères inférieurs. Leur formule polycyclanique (par exemple, formule I pour le trimère) faisant des polyindènes des corps à 6, 8, 10, 12 . . . atomes de carbone dans l'anneau (vielgliedrige Ringe), à priori bien possible d'après les travaux de Ruzicka et ses collaborateurs, explique difficilement les résultats obtenus par l'auteur même dans la détermination des viscosités des acides polystyréniques (16, p. 217), les moments dipolaires déterminés par Gallay (9), nos oxydations par l'acide nitrique et la résistance du trimère à la déhydrogénation catalytique.

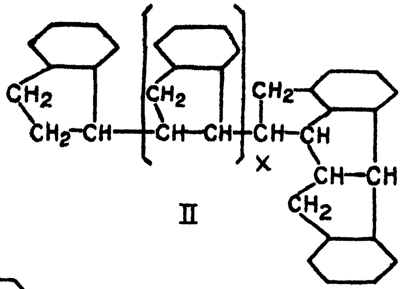
Nous acceptons la formule non saturée de Whitby et Katz pour les produits intermédiaires, produits directs de la réaction à chaîne, mais nous devons chercher une formule saturée pour les polyindènes, conformément à leurs propriétés, et basée surtout sur la transposition du 2-(α-hydrindyl)-indène en diindène saturé par simple chauffage.

Une formule II théoriquement possible, calquée sur les cas analogues des dimères de l'α-méthyl-styrène (3) et du diphényl-éthylène asymétrique (4), doit être éliminée par le fait que déjà le 2-(α-hydrindyl)-indène III ne se transpose pas en IV (2), car le composé polycyclique IV ne peut pas être stable pour des raisons de tension dans l'anneau, comme l'ont démontré Braun et Anton (6) en trouvant que des dérivés du type V ne se forment pas même par la réaction de Friedel et Crafts.

Une deuxième formule possible pour les polyindènes résulte du travail de Alder et Stein (1) qui ont prouvé que le dicyclo-pentadiène obtenu par polymérisation spontanée du cyclopentadiène n'est pas un dérivé symétrique du cyclobutane VI, tel que jusqu'ici considéré, mais bien un corps de constitution asymétrique VII. En appliquant ce cas à l'indène, nous aurions pour le diindène saturé la formule VIII (benzylène-1, 2-phénylène-3, 5-cyclopentane) et pour les polyindènes une formule correspondante IX, dans laquelle la chaîne des $x + 1$ unités indéniques serait fixée sur le groupement CH médian des deux unités formant la fin asymétrique de toute la chaîne. On ne peut cependant pas appliquer la polymérisation de deux molécules de cyclopentadiène sans aucune réserve au cas de l'indène, car dans le premier cas il y a un système de doubles liaisons conjugées alicycliques qui fait défaut dans l'anneau indénique. D'ailleurs une formule analogue à IX pour les polystyrènes est, à priori, impossible.



I



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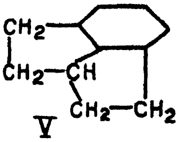
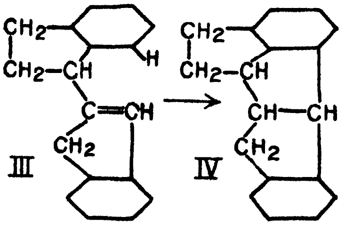
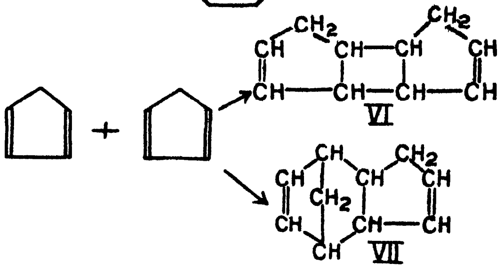


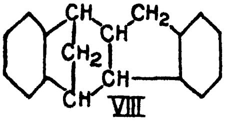
V



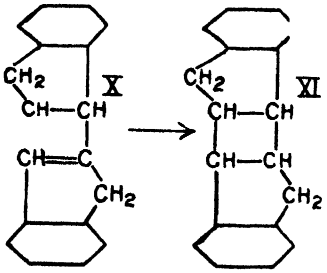
III IV



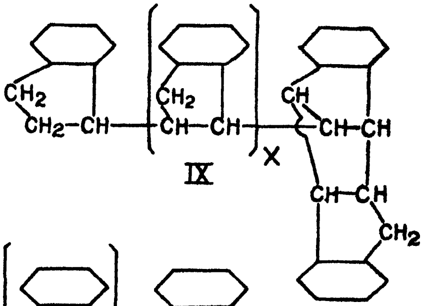
VI VII



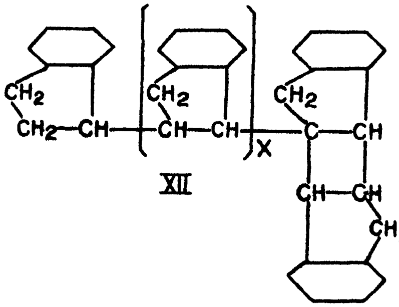
VIII



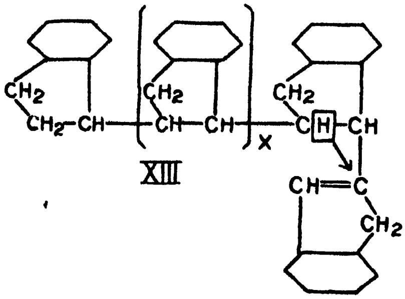
X XI



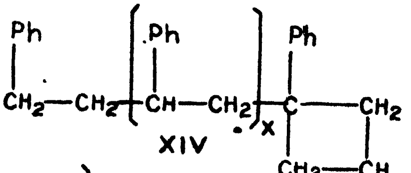
IX



XII



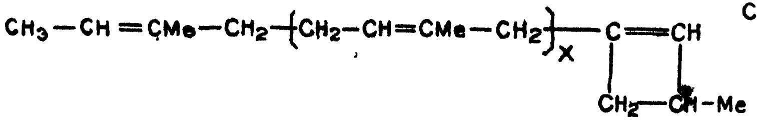
XIII



XIV

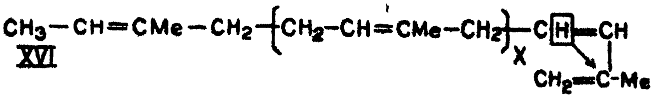
$$CH_2(Ph)-CH_2\{CH(Ph)-CH_2\}_x C(Ph)-CH_2-CH(Ph)-CH_2$$

XV



$$CH_3-CH=CMe-CH_2\{CH_2-CH=CMe-CH_2\}_x\,C=CH$$
$$CH_2-CH-Me$$

XVI



$$CH_3-CH=CMe-CH_2\{CH_2-CH=CMe-CH_2\}_x\,C\boxed{H}=CH$$
$$CH_2=C-Me$$

Enfin une troisième possibilité de cyclisation est celle qui conduit à la formation d'un dérivé du truxane. La constitution du truxane XI étant prouvée par synthèse (Stobbe et collaborateurs), nous proposons la formule XII pour les polyindènes.

Cette formule est conforme aux propriétés des polyindènes, à savoir: le caractère saturé, la résistance relative à l'oxydation, la possibilité de donner avec l'acide nitrique des produits dinitrés et dicarboxylés, et surtout l'asymétrie moléculaire qui explique l'état amorphe des polyindènes et qui fait comprendre les résultats obtenus par Gallay (9) dans ses déterminations des moments dipolaires des polyindènes supérieurs. Quoique cet auteur n'ait pas travaillé sur les termes inférieurs et qu'il interprête l'augmentation du moment polaire avec le degré de polymérisation en faveur d'une double liaison, nous croyons que l'asymétrie observée par lui s'explique très bien par la formule XII. D'ailleurs Ostwald et Riedel (13) remarquent que: "Eine Erklärung der Zunahme des Momentes ist aufs Engste verknüpft mit der Vorstellung, die man sich über die Konstitutionsänderungen macht, die bei der Polymerisation eintreten. Solange die Konstitutionstheorie dieser Polymerisation noch umstritten ist (siehe die entgegengesetzten Anschauungen von Whitby und Staudinger, Gallay loc.cit.), erscheint der Versuch einer konstitutionschemischen Deutung der Momentzunahme mit steigendem Polymerisationsgrad verfrüht."

De plus, la formule XII n'est pas en désaccord avec les mesures de viscosité de Staudinger et collaborateurs, car les polyindènes ainsi constitués conservent un caractère essentiellement filamentaire, et la petite boucle formée par les deux dernières unités indéniques de la chaîne n'influencera pas de façon notable la viscosité et les autres propriétés du filament. D'ailleurs Staudinger (16, p. 223) avait déjà exprimé l'idée de tels réarrangements à la fin de la chaîne sous l'action de catalyseurs, sans toutefois les préciser.

Cette nouvelle hypothèse constitutionnelle, faisant des polyindènes des filaments simples avec une boucle terminale, peut très bien être appliquée aussi au cas des polystyrènes pour lesquels nous voudrions proposer la formule XIV. Une constitution analogue des polyprènes, en particulier du caoutchouc XV, formé à partir de XVI par migration d'hydrogène et cyclisation, serait aussi très plausible à la suite des travaux de Karrer et collaborateurs (10) sur d'autres dérivés polypréniques naturels, tels que la zéaxanthine, la xanthophylle et la vitamine A.

Mécanisme de polymérisation

Nous acceptons avec Staudinger, Chalmers (7) et Semenoff (14) que la polymérisation soit une réaction à chaîne, en l'accompagnant cependant d'un déplacement atomique. L'énergie libérée pendant la combinaison de deux molécules peut se manifester sous une autre forme que celle des liaisons terminales libres préconisées par Staudinger. Ainsi on peut supposer que cette énergie soit cédée à une double liaison à l'extrémité du polymère formé et que celle-ci par son activation provoque immédiatement l'addition d'une autre molécule de monomère avec déplacement atomique, tel que formulé par Whitby et Katz. L'énergie mise en jeu dans cette nouvelle combinaison active à son tour la double liaison de la molécule résultante, celle-ci additionne comme la précédente, etc.

$$M_1 \longrightarrow M'_1$$

$$M'_1 + M_2 \longrightarrow M_1 M'_2$$

$$M_1 M'_2 + M_3 \longrightarrow M_1 M_2 M'_3, \text{ etc.}$$

La chaîne, réactivée chaque fois par l'énergie résultant de l'addition d'un nouveau chaînon, conserve son aptitude à réagir et continue à progresser jusqu'à ce qu'elle soit arrêtée par un accident, qui se manifeste par une réaction secondaire sous la forme d'une cyclisation entre les deux dernières unités de la chaîne; la formule XIII représente cette cyclisation qui donne ainsi les polyindènes XII.

Le nombre de molécules mises en jeu dépend en premier lieu de l'énergie excitante, mais il est aussi fonction des facteurs qui peuvent accroître les chances de cyclisation, tels que le degré de polymérisation, les chocs intermoléculaires ou sur les parois du récipient, ou toute autre manifestation de l'énergie du milieu ambiant. Ainsi la tendance à la cyclisation croît avec la température au détriment de la force polymérisante, comme le démontrent nettement la transposition du diindène non saturé en diindène saturé et la diminution graduelle du degré de polymérisation avec l'élévation de la température.

Pour expliquer maintenant les résultats négatifs obtenus par Staudinger dans ses essais d'addition de styrène au di- et tri-styrène, et nos propres insuccès dans le cas analogue de la série indénique, nous n'avons qu'à remarquer que les conditions de la réaction à chaîne n'existent pas dans ces cas. L'énergie nécessaire à la réaction n'est pas libérée par une combinaison antérieure, puisque nous partons de dimères et trimères déjà formés. Cette énergie doit nécessairement provenir du milieu ambiant, elle peut ne pas être suffisante ou être d'une autre forme et se manifester d'une façon différente. C'est ce que nous avons d'ailleurs prouvé dans le cas du diindène non saturé.

Partie Expérimentale

Préparation du diindène non saturé

On porte à ébullition un mélange de 100 g. d'indène, 100 cc. d'acide chlorhydrique et 10 g. de pierre ponce. Les temps de chauffage et les concentrations initiales d'acide chlorhydrique sont donnés dans le tableau I. On décante la couche indénique, on neutralise par agitation avec une solution de carbonate de sodium 5%, on sèche sur le chlorure de calcium, on distille les produits de réaction dans le vide et on redistille à 1 ou 2 mm. la fraction correspondante au diindène, qui passe à 145-160° C. On cristallise de l'acide acétique glacial, on lave à l'acide acétique dilué, puis avec du carbonate de sodium 5% et finalement à l'eau. On sèche dans le vide. On obtient ainsi un produit incolore de P.F. 56° C. et de P.M. 224 (calculé pour $(C_9H_8)_2$: 232). Les rendements sont donnés dans le tableau I.

Préparation du "triindène"

On chauffe des mélanges de quantités respectivement égales et équimoléculaires d'indène et de diindène non saturé en tubes scellés et à l'obscurité à 195°, 215° et 235° C. pendant un temps variable, tel qu'exposé dans le tableau II. On sépare ensuite les différents constituants par distillation fractionnée à 2 mm. Fraction 1: indène, P.E. 35-40° C.: fraction 2; diindène, P.E. 160-175° C., huile jaunâtre visqueuse; fraction 3; "triindène", P.E. 215-240° C., huile orangée, très visqueuse, se solidifiant très vite sous forme résineuse: fraction 4; polyindène, P.E. 240-275° C., produit vitreux: fraction 5; résidu.

La fraction 3 pulvérisée et traitée par quatre fois son poids d'éther à 0° C. laisse après repos de 24 h. un dépôt cristallin (8-10%). On filtre et on lave à l'éther. La substance insoluble, cristallisée à plusieurs reprises du benzène, forme de longues aiguilles incolores de P.F. 214° C. La solution éthérée est évaporée et le "triindène" ainsi débarrassé de cette substance étrangère est repris par un grand volume d'alcool absolu à chaud. On obtient par refroidissement un produit jaune pâle, parfaitement homogène, mais amorphe, de P.L. 70-71° C.; C, 93.01; H, 6.74% (calculé C_9H_8: C, 93.10; H, 6.90%). P.M. 357, 350 (calculé $(C_9H_8)_3$: 348). Rendement: 42 g. de la fraction 3 donnent 27 g. de "triindène" purifié. Par évaporation graduelle des eaux-mères dans le vide, on récupère trois fractions inférieures, P.L. 62° C. et P.M. 306; P.L. 54-55° C. et P.M. 244; P.L. 50-52° C. et P.M. 225.

La fraction 4 traitée de la même façon que la précédente donne les résultats suivants: 10 g. de produit brut fournissent 3 g. de la substance de P.F. 214° C., 4.2 g. d'un polyindène de P.L. 80° C. et 2.5 g. de "triindène" de P.L. 65-66° C.

Le résidu 5 (8 g.) est partiellement soluble dans l'éther. Après filtration et addition d'alcool, il précipite 4 8 g. d'un polyindène supérieur au "triindène", P.L. 90° C. La portion insoluble dans l'éther se dissout en grande partie dans le benzène à chaud et cristallise par refroidissement, P.F. 214° C. (2.5 g.). Il reste cependant sur le filtre 0.6 g. d'un produit insoluble dans le benzène, de P.F. > 350° C., considéré comme truxène.

Preuve de la non-homogénéité du "triindène"

1. *"Triindène" synthétique*

a. Par dissolution fractionnée. On traite 4 g. de triindène de P.L. 70° C. par 20 cc. d'alcool absolu à chaud. On décante la solution et on refroidit: il se forme un précipité de P.L. 72° C. Le résidu du premier traitement repris dans les mêmes conditions par 10 cc. d'alcool absolu donne un second précipité du P.L. 74-75° C. En répétant la même opération à trois reprises sur le résidu, on obtient trois nouvelles fractions de P.L. respectivement 78-80°, 85-87° et 90-92° C. Par concentration des eaux-mères de ces différents traitements, on obtient une fraction inférieure de P.L. 63-64° C.

b. Par précipitation fractionnée. On dissout 3 g. de "triindène" de P.L. 70° C. dans 20 cc. d'éther et on y ajoute à 0° avec agitation 40 cc. d'alcool absolu. On obtient ainsi un précipité de P.L. 87-88° C. et de P.M. 423.

On ajoute encore de l'alcool au filtrat et on concentre par évaporation partielle à froid: on obtient un second précipité de P.L. 77-78° C. et de P.M. 387. En concentrant davantage, on obtient encore trois autres dépôts de P.L. 74-75°, 69-70° et 64-65° C. et de P.M. respectivement 370, 331 et 311.

Après une reprise de la précipitation fractionnée sur une plus grande échelle (à partir de 25 g. de "triindène" de P.L. 70° C.), les différentes fractions obtenues sont de nouveau soumises au même traitement, mais encore là elles montrent un manque d'homogénéité. Une de ces fractions, de P.L. 73-74° C. et de P.M. 362, donne trois sous-fractions de P.L. 83°, 77° et 69° C. Une autre fraction de P.L. 85-86° C. et de P.M. 408 en fournit quatre de P.L. respectivement 98-100°, 90-92°, 86-88° et 76-78° C.

2. *"Triindène" de décomposition pyrolytique*

On polymérise d'abord l'indène avec le pentachlorure d'antimoine suivant la méthode de Whitby et Katz (31): P.L. 205° C. et P.M. 1354. On soumet ce polyindène à la distillation pyrolytique suivant les mêmes auteurs (30). Le "triindène" du P.L. 70° C. ainsi obtenu après purification est soumis à dissolution et précipitation fractionnée comme le précédent. Il donne approximativement les mêmes sous-fractions.

Essais montrant que le diindène non saturé n'intervient pas dans la synthèse du "triindène"

Dix grammes d'indène, 10 g. de diindène non saturé, un mélange de 10 g. d'indène et de 10 g. de diindène, et un mélange de 10 g. d'indène et de 10 g. de kérosène du P.E. 210-220° C. sont chauffés en tubes scellés pendant trois jours à 215° C. L'indène, le diindène et le kérosène respectivement sont ensuite soigneusement enlevés par distillation à 2 mm. Les polymères restant dans le ballon sont alors traités exactement de la même façon, à savoir: dissolution dans trois fois le poids d'éther par rapport au poids des polymères, puis précipitation par trois volumes d'alcool absolu. Le précipité obtenu, légèrement collant, est de nouveau repris par trois fois son poids d'éther et précipité par trois fois son volume d'alcool donnant ainsi la fraction 1; par évaporation à froid du filtrat au deux tiers de son volume, on obtient la fraction 3. Les eaux-mères de la première précipitation sont aussi évaporées à froid, d'abord aux deux tiers, donnant la fraction 2, puis au quart, laissant la fraction 4. Toutes ces fractions sont ensuite séchées dans le vide. Les quantités, les P.L. et les P.M. des produits obtenus figurent au tableau III.

Transposition du diindène non saturé en diindène saturé

L'huile jaunâtre visqueuse qui forme la fraction 2 (P.E. 160-175° C. à 2-3 mm.) dans la préparation du "triindène" n'a pas pu être amenée à la cristallisation, malgré tous les essais de purification avec les solvants connus du diindène non saturé. Ceci laissait prévoir une certaine transformation que les mesures d'absorption de brome ont confirmée: cette huile contient une forte proportion d'un hydrocarbure saturé.

Cette constatation nous a amené à étudier une transposition possible du diindène non saturé en diindène saturé (truxane). Afin de le confirmer, nous avons chauffé 10 g. de diindène non saturé en tube scellé à 185° et 215° C. pendant respectivement trois et quatre jours. Les produits de réaction ont été distillés (13 mm.) et les fractions de P.E. 206-207° C. ont été soumises à la bromuration avec les résultats indiqués dans le tableau IV. Dans le premier cas, il s'est formé en même temps 2 g. de polyindènes et dans le deuxième 4.2 g.

Les propriétés de ce diindène saturé furent ensuite comparées avec celles du truxane synthétique de Stobbe et Zschoch (24): les deux produits semblent identiques (voir partie théorique). Nous n'avons cependant pas encore réussi à les cristalliser, difficulté que Stobbe et Zschoch ont déjà signalée.

Bromuration

1. *Préparation d'un dérivé bromé du "triindène"*

On dissout 3 g. de "triindène" du P.L. 70° C. dans 15 cc. de chloroforme et on y ajoute à 0° C. 1.5 g. de brome (quantité calculée pour deux atomes par mol.-g.) dissous dans 10 cc. de chloroforme. On abandonne à froid pendant 24 h. Il y a dégagement d'acide bromhydrique. On évapore le chloroforme, on reprend par l'éther (15 cc.) et on filtre le résidu: 0.5 g. de P.L. 160° C. Le filtrat précipité graduellement par addition d'alcool et concentration partielle donne les quatre fractions suivantes: I. P.L. 145°, Br: 34.2%; II. P.L. 115°; III. P.L. 90°; IV. P.L. 80° C. Cette dernière fraction ne contient que très peu de brome.

En reprenant la bromuration avec une quantité de brome calculée pour six atomes, on obtient un meilleur rendement en fractions supérieures, peu solubles dans l'éther. Après filtration, dissolution dans le benzène et précipitation par addition d'alcool, on obtient une poudre jaune de P.L. 163-166° C. Br, 40.14% (calculé pour $C_{27}H_{21}Br_3$: Br, 40.99%).

2. *Détermination de l'absorption de brome*

On emploie la méthode de McIlhiney (12), pour déterminer à la fois le brome total consommé et le brome dégagé sous forme d'acide bromhydrique. Les bromurations sont faites à l'obscurité à des températures déterminées, avec des solutions 0.08 N, $N/3$ et N de brome dans le tétrachlorure de carbone anhydre, pendant 18 h. On titre alors le brome en excès avec le thiosulphate de sodium $N/10$ après addition d'iodure de potassium et on obtient la quantité totale de brome consommée par différence avec un essai à blanc. On ajoute ensuite de l'iodate de potassium qui met en liberté l'iode correspondant à l'acide bromhydrique formé: en titrant de nouveau avec du thiosulphate de sodium, on obtient la quantité de brome substitué. Les résultats sont donnés dans le tableau IV.

Les thermopolymères employés pour la bromuration ont été préparés par chauffage de l'indène en tube scellé à 200° C. pendant trois jours, et purifiés par dissolution dans l'éther et précipitation par l'alcool. *a.* P.L. 102° C. et P.M. 451. *b.* P.L. 160° C. et P.M. 885.

Le polyindène provenant d'une décomposition pyrolytique d'un polyindène supérieur a été préparé de la façon suivante: On forme d'abord un polyindène catalytique par réaction du pentachlorure d'antimoine sur l'indène en solution chloroformée et on le purifié par précipitation répétée d'une solution benzénique par l'alcool absolu. P.L. 205° C., et P.M. 1354. On soumet ensuite ce polyindène à une distillation pyrolytique à 2 mm., suivant la méthode de Whitby et Katz (30). Le distillat est fractionné par nouvelle distillation en indène, diindène et "triindène". Le résidu de cette seconde distillation, repris par l'éther et précipité par l'alcool donne une poudre jaune de P.L. 120° C. et de P.M. 546. C'est cette fraction qui a été employée pour la mesure de l'absorption de brome.

Les polyindènes catalytiques ont été obtenus par polymérisation de l'indène avec du pentachlorure d'antimoine suivant la méthode de Whitby et Katz (31) et avec l'acide sulfurique concentré suivant Kràmer et Spilker (11). Le fractionnement a été fait par dissolution dans le chloroforme et précipitation graduelle par l'alcool.

Polyindènes catalytiques par l'acide sulfurique: 1ère fraction: P.L. 185° C. et P.M. 1357. 2ième fraction: P.L. 168° C. et P.M. 1153.

Polyindènes catalytiques par le pentachlorure d'antimoine: Avant fract. P.L. 198° C. et P.M. 1146. 1ère fraction: P.L. 220° C. et P.M. 1860; 2ième fract. P.L. 210-215° C. et P.M. 1537; 3ième fract. P.L. 180° C. et P.M. 1080; 4ième fract. P.L. 165° C. et P.M. 892. C'est la première fraction qui a servi aux essais de bromuration dans chacun des deux cas. A titre de comparaison, quelques bromurations ont été faites avec du chloroforme comme solvant.

Autres preuves pour le caractère saturé du "triindène" et des polyindènes

1. *Essais d'addition de chlorure de nitrosyle*

a. Sur l'indène: On dissout 5 cc. d'indène dans 12 cc. d'acide acétique glacial et on y ajoute 6 cc. de nitrite d'amyle. On refroidit à 0° C. et on ajoute goutte à goutte un mélange de 8 cc. d'acide chlorhydrique concentré et 8 cc. d'acide acétique glacial. On abandonne à froid pendant 30 min. La solution prend une teinte verdâtre et laisse déposer bientôt une abondante poudre cristalline. On filtre, on lave à l'alcool et on obtient ainsi 1.5 g. d'un produit incolore. On purifie par cristallisation d'un grand volume d'acétone. Il y a cependant perte notable, due à l'instabilité du produit. P.F. avec décomposition: 148-150° C.; Cl, 19.57% (calculé pour C_9H_8NOCl: Cl, 19.53%).

b. Sur le diindène non saturé: On mélange 5 g. de diindène avec 4 cc. de nitrite d'amyle et 12 cc. d'acide acétique glacial. On ajoute alors à 0° goutte à goutte un mélange de 3 cc. d'acide chlorhydrique concentré et 10 cc. d'acide acétique glacial. Au bout de 20 min., on verse le tout sur de la glace pilée et on extrait aussitôt à l'éther. On obtient ainsi une solution vert foncée. On décante l'extrait éthéré, on lave jusqu'à neutralisation avec une solution aqueuse à 5% de carbonate de sodium, on lave à l'eau, on sèche sur le chlorure de calcium et on filtre. On laisse évaporer l'éther dans le vide. On obtient ainsi une huile vert foncée, qui se montre très instable, car elle se transforme spontanément en une huile brune, visqueuse, qui ne se solidifie pas. Il s'agit sans doute d'un nitroso-chlorure de diindène, parce que l'huile contient de l'azote et du chlore et que le produit vert donne en solution alcoolique avec du nitrate d'argent alcoolique un précipité de chlorure d'argent et libère l'iode d'une solution d'iodure de potassium, réactions caractéristiques des nitroso-chlorures.

c. Sur le "triindène": Deux essais faits sur un "triindène" du P.L. 75° C., l'un dans les mêmes conditions que les précédentes, l'autre par dissolution du "triindène" dans le nitrite d'amyle et agitation au contact d'acide chlorhydrique concentré, ne produisent aucun résultat positif: on récupère le "triindène" non attaqué.

2. *Essais de condensation avec le nitrite d'amyle*

a. Sur le "triindène" non fractionné, de P.L. 70° C. On dissout 3 g. de "triindène" dans 15 cc. d'éther et on y ajoute 3 cc. de nitrite d'amyle. On verse alors le tout goutte à goutte et avec agitation dans une solution alcoolique d'éthylate de Na (5 g. de Na dans 100 cc. d'alcool éthylique). On laisse au repos pendant quelques heures à température ordinaire, on verse dans l'eau, on acidule par l'acide chlorhydrique, on extrait au chloroforme, on sèche la solution chloroformée sur le chlorure de calcium, on filtre et on évapore le solvant. On reprend le résidu huileux par l'éther de pétrole. Il se sépare ainsi très peu (0.15 g.) d'un produit qui, après purification par lavage à l'éther, dissolution dans le chloroforme et précipitation par l'éther de pétrole, fond à 200° C. Ce corps donne les réactions des composés isonitrosés et il correspond analytiquement au dérivé connu du diindène: N, 5.13% (calculé pour $C_{18}H_{15}NO$: N, 5.4%); P.M. ébullioscopiquement dans le chloroforme, 285 (calculé: 262). P.F. du dérivé isonitrosé connu du diindène, 201° C. Par évaporation de l'éther de pétrole des eaux-mères, reprise par l'éther et précipitation par l'alcool, on récupère le "triindène" inaltéré, P.L. 78-80° C. Le "triindène" ne réagit donc pas avec le nitrite d'amyle, mais il contient un peu de diindène non saturé.

b. Sur un thermopolymère de P.L. 102° C. et de P.M. 451. On traite 3 g. de ce thermopolymère par le nitrite d'amyle dans les mêmes conditions que précédemment; il ne se forme que des traces d'un composé nitrosé, considéré comme dérivé du diindène non saturé ou de l'indène, tandis que les polyindènes inattaqués sont récupérés.

3. *Essais de condensation avec la benzaldéhyde et la para-diméthyl-amino-benzaldéhyde*

Ces condensations sont essayées en milieu alcoolique absolu (préalablement desséché sur des tournures de calcium) avec l'éthylate de sodium ou la potasse méthyl-alcoolique comme agent de condensation, suivant les méthodes de Thiele (26) et de Bernthsen (5); mais dans l'un et l'autre cas, le "triindène" demeure inaltéré.

4. *Essais de polymérisation*

a. Par la chaleur: On chauffe 4 g. de "triindène" de P.L. 70° C. en tube scellé pendant 8 et 15 jours à 240°, 280° et 310° C. On additionne ensuite 15 cc. d'éther, on laisse au repos pendant quelques heures à 0° et on filtre. La partie insoluble dans l'éther est reprise à chaud par un peu de benzène; il y a dissolution entière (sauf dans le cas du chauffage à 310° C. où on constate la présence d'une faible quantité de truxène insoluble) et cristallisation, par refroidissement, de la substance déjà mentionnée: P.F. 213-214° C. La partie soluble dans l'éther précipite par addition de quatre fois son volume d'alcool et concentration partielle: on y récupère le "triindène". Les résultats plus détaillés sont réunis dans le tableau V, qui montre que la quantité de la substance de P.F. 214° C. formée augmente avec la température et le temps de chauffage. A 310° C., la transformation est plus avancée, il y a une odeur piquante et une pression dans le tube; on ne récupère plus alors de "triindène" par addition d'alcool à la solution éthérée.

b. Par l'acide sulfurique concentré: On dissout 4 g. de "triindène" dans 10 cc. de benzène et on y ajoute lentement et avec agitation 5 cc. d'acide sulfurique concentré. Il y a aussitôt coloration rouge intense. On laisse 10 h. au repos. On refroidit à 0° C. et on y ajoute lentement 30 cc. d'alcool absolu qui provoque précipitation. On redissout dans l'éther et on reprécipite par l'alcool. P.L. 74-75° C. et P.M. 367. Il n'y a donc pas eu polymérisation.

c. Par le pentachlorure d'antimoine: Action sur le "triindène" non fractionné de P.L. 70° C.: A une solution de 4 g. de "triindène" dans 25 cc. de chloroforme on ajoute 4 cc. d'une solution à 20% du pentachlorure d'antimoine dans le chloroforme, on porte à 40° C. pendant une heure et on laisse une nuit au repos. En traitant alors la solution à froid par quatre fois son volume d'alcool absolu, on obtient 1.5 g. de dépôt brun, P.L. 110° C. En répétant deux fois la même opération (dissolution dans un peu de chloroforme et précipitation par addition de quatre fois le volume d'alcool), on obtient environ 0.5 g. d'une poudre jaune de P.L. 148-150° C. Par concentration des eaux-mères de ces différentes précipitations, on récupère la majeure partie du "triindène", P.L. 80° C. Le produit de P.L. 148-150° C. repris (sur une plus grande échelle) par le chloroforme et reprécipité graduellement par l'alcool a donné les trois fractions suivantes: I. P.L. 175° C. et P.M. 817; II. P.L. 155° C. et P.M. 673; III. P.L. 140-142° C. et P.M. 566. Le faible rendement obtenu laisse croire cependant que cette polymérisation n'est pas due au "triindène" lui-même, mais bien à la faible quantité de diindène non saturé qu'il contient. Le diindène, en effet, sous l'influence du pentachlorure d'antimoine se polymérise jusqu'à un degré d'environ P.M. 1200 (30). On peut alors admettre que le peu de polymère en question, obtenu en traitant le "triindène" de P.L. 70° C. par le pentachlorure d'antimoine, n'est qu'un mélange des produits de polymérisation du diindène non saturé présent comme impureté et des fractions polyindéniques supérieures initialement présentes.

Action sur un "triindène" débarrassé le plus possible du diindène non saturé: On dissout 0.5 g. d'une fraction triindénique soigneusement préparée, de P.L. 84-85° C., dans 5 cc. de chloroforme, on y ajoute 0.5 cc. d'une solution à 20% du pentachlorure d'antimoine dans le chloroforme et on laisse au repos pendant 18 h. On précipite alors par addition à 0° C. de 20 cc. d'alcool absolu. On filtre, on lave à l'alcool et on sèche dans le vide. On obtient ainsi 0.28 g. d'un polyindène de P.L. 93-95° C. Par concentration des eaux-mères, on obtient un nouveau dépôt (0.16 g.) de P.L. 85° C. On fait dans les mêmes conditions un essai à blanc en dissolvant 0.5 g. du "triindène" de P.L. 84-85° C. dans 5 cc. de chloroforme et en précipitant à 0° C. par 20 cc. d'alcool absolu; on obtient ainsi après filtration, lavage et séchage 0.20 g. d'un polyindène de P.L. 89-90° C.; en concentrant les eaux-mères, on récupère 0.22 g. de P.L. 83-84° C. La hausse du P.L. dans les deux cas est donc due uniquement au fractionnement par l'alcool, et non, dans le premier cas, à une polymérisation par le pentachlorure d'antimoine. Dans l'un et l'autre cas, on rassemble les deux fractions et on prend le P.M. du mélange. Premier cas: traitement par le pentachlorure d'antimoine, P.M. 408; deuxième cas: essai à blanc, P.M. 392.

On fait de même un essai de polymérisation par le pentachlorure d'antimoine d'un "triindène" préalablement débarrassé du diindène non saturé par réaction avec le nitrite d'amyle. Encore là le résultat est négatif.

5. *Densités et réfractions moléculaires*

On détermine la réfraction moléculaire de l'indène, du diindène non saturé, du "triindène" et de quelques polymères supérieurs, en opérant avec le réfractomètre Abbé et en utilisant la formule de Lorentz et Lorenz. Les mesures sont faites à 20° C. Les résultats sont donnés dans le tableau VI.

Oxydation

1. *Avec le permanganate de potassium*

a. En milieu acide: On dissout 2 g. de "triindène" de P.L. 74° C. dans 25 cc. de benzène et on agite pendant huit heures avec une solution acide de permanganate de potassium à 2%. On ajoute ensuite assez d'anhydride sulfureux pour décolorer l'excès de permanganate. On décante la solution benzénique surnageante et on l'agite avec une solution de carbonate de sodium à 5% dans le but d'extraire les acides (il n'y en a que des traces). La solution benzénique concentrée, additionnée d'alcool absolu et de nouveau concentrée, donne un premier dépôt de 0.4 g., P.L. 87-88° C., puis par évaporation plus avancée un second dépôt de 0.24 g., P.L. 75-77° C. et finalement par évaporation totale un résidu de P.L. inférieur à 75° C. On récupère ainsi différentes fractions du "triindène" de départ.

b. En milieu alcalin: On chauffe à ébullition pendant quatre heures 1 g. de "triindène" avec une solution aqueuse de permanganate de potassium (calculée pour un atome-gramme d'oxygène) et de potasse. La solution aqueuse ne se décolore pas et il ne se forme que très peu de bioxyde de manganèse. Le "triindène" résiste à l'oxydation dans ces conditions.

2. *Avec l'acide chromique*

On dissout 2 g. de "triindène" de P.L. 75° C. dans 25 cc. d'acide acétique glacial et on y ajoute à 75° C. 3 g. d'anhydride chromique préalablement dissous dans de l'acide acétique. On laisse au repos pendant une nuit. On distille alors la plus grande partie de l'acide acétique dans le vide, on dilue le résidu avec un grand volume d'eau et on extrait au benzène. On sèche sur le chlorure de calcium, on filtre et on évapore le benzène. On obtient ainsi un produit résineux, rouge orangé. On le redissout dans l'alcool à chaud, on y ajoute 0.5 g. de chlorhydrate de semicarbazide et 0.5 g. d'acétate de potassium préalablement dissous dans de l'alcool dilué. On porte à ébullition pendant quatre heures. Après refroidissement, on obtient un faible précipité (0.2 g.) d'un produit orangé de P.F. non net 120-123° C. qui ne contient cependant pas d'azote. On évapore l'alcool des eaux-mères et on lave le résidu avec un grand volume d'eau afin d'enlever l'excès de chlorhydrate de semicarbazide et d'acétate de potassium. On obtient ainsi 1 g. d'un corps jaune de P.L. 85° C., ne contenant que très peu d'azote et ne renfermant que des traces d'acides, parmi lesquels on peut caractériser l'acide phtalique. Il n'y a donc pas eu formation d'α-hydrindone ou d'α-hydrindyl-hydrindone.

L'oxydation répétée en portant à l'ébullition la solution chromique-acétique pendant six heures donne des résultats identiques aux précédents.

3. *Avec l'acide nitrique* (*d*, *1.25*)

Des échantillons de "triindène" et de polyindènes thermiques et catalytiques sont portés à l'ébullition pendant trois à quatre heures avec 10 fois leur poids d'acide nitrique (*d*, 1.25). On laisse ensuite refroidir, on ajoute un volume égal d'eau, on filtre et on lave abondamment à l'eau. Le produit jaune orangé resté sur le filtre est repris par l'acétone dans laquelle une très faible partie est insoluble. P.F. > 425° C. Ce produit est insoluble dans les solvants ordinaires, il contient de l'azote, mais n'est pas de nature acide (N, 5.98%). Par addition d'un volume égal d'alcool à l'acétone et par évaporation graduelle il précipite à volonté plusieurs fractions d'un produit azoté de nature acide, que l'on purifie par dissolution dans la potasse ou l'ammoniaque dilué, filtration et reprécipitation par l'acide chlorhydrique dilué. Après filtration, lavage à l'eau et nouvelle purification par l'acétone et l'alcool, on obtient des produits dont les points de liquéfaction, les P.M. et les analyses sont donnés dans le tableau VII. Ces produits sont insolubles dans l'éther et le benzène, peu solubles dans le chloroforme et très solubles dans l'acétone. D'après la réaction de Konovalow, négative, les groupements NO_2 doivent être fixés sur des anneaux aromatiques.

Les eaux-mères aqueuses, neutralisées par la soude et de nouveau acidulées par l'acide chlorhydrique dilué, sont évaporées à sec. On peut extraire l'acide phtalique du résidu par l'alcool absolu et le purifier par sublimation. On constate que les rendements en acide phtalique sont plus forts pour le "triindène" que pour les polyindènes catalytiques.

Deux grammes de diindène non saturé oxydé dans les mêmes conditions donnent 0.25 g. d'un produit nitré analogue au précédent. P.M. 390; N, 7.19%. Les eaux-mères donnent par évaporation un résidu en majeure partie constitué par de l'acide phtalique.

Deux grammes de diindène saturé, provenant de la transposition du diindène non saturé à 215° C., fournissent les mêmes produits d'oxydation, avec cependant un peu plus de produit azoté (0.32 g.).

Le truxane synthétique se comporte de la même façon.

4. *Avec le mélange nitrique-sulfurique*

Des échantillons de polyindènes thermique et catalytique (acide sulfurique) sont portés à l'ébullition avec 60 cc. d'un mélange à parties égales d'acide nitrique concentré et d'acide sulfurique concentré. Une grande partie des polyindènes entre en solution. On filtre sur de l'amiante, on lave, on sèche et on purifie le produit acide et azoté comme dans le cas précédent. Les constantes et les analyses sont données dans le tableau VIII. Par addition d'eau au filtrat, il précipite une très faible partie des mêmes produits. Les eaux-mères ne contiennent pratiquement pas d'acide phtalique.

Essai de déhydrogénation catalytique du trimère de l'indène

Le noir de palladium activé est préparé par réduction du chlorure de palladium avec l'acide formique en milieu alcalin (25).

On chauffe 1 g. de "triindène" de P.L. 74° C. avec 0.3 g. de noir de palladium fraîchement activé pendant six heures à 300-310° C. en tube scellé. On traite alors par un peu d'éther pour dissoudre le "triindène" non attaqué, on filtre et on lave à l'éther. On traite le résidu par un mélange d'acide nitrique et chlorhydrique dilués pour dissoudre le palladium; il reste ainsi 0.24 g. de la substance de P.F. 214° C., que l'on purifie par recristallisation du benzène. Un essai à blanc dans les mêmes conditions sur un autre gramme de "triindène", mais sans catalyseur, fournit 0.22 g. de la même substance. Il n'y a donc pas eu de déhydrogénation catalytique.

Dédoublement pyrolytique du "triindène"

On chauffe 10 g. de "triindène" de P.L. 70° C. à pression ordinaire sur un bain d'alliage Wood. On note la température du bain et celle du liquide dans le ballon. Le "triindène" ne commence pas à se dépolymériser avant d'avoir atteint une température de 335° C. pour le bain et 325° C. pour le liquide. La dépolymérisation devient plus active à une température légèrement supérieure. On chauffe ainsi pendant trois heures. On recueille comme distillat 3-4 g. d'un liquide qui a l'odeur de l'indène et qui bout à 179-180° C. par redistillation. On fait ensuite le vide et il passe à 140-150° C., sous 2 mm., environ 1 g. d'une huile visqueuse de laquelle ne peut être isolée qu'une faible quantité de l'α-hydrindyl-indène (P.F. 55° C.), la majeure partie de l'huile étant constituée de diindène saturé. Le résidu dans le ballon à distillation est traité par 25 cc. d'éther qui n'en dissout que très peu. On filtre et on ajoute de l'alcool absolu au filtrat. Il précipite ainsi 0.5 g. d'un corps jaune de P.L. 74-75° C. et de P.M. 365 ("triindène" non transformé). La partie insoluble dans l'éther est reprise par 50 cc. de benzène à chaud. On filtre et il précipite par refroidissement 2.0 g. d'un corps jaune pâle, qui, après recristallisation, fond à 214° C. (substance déjà mentionnée). La partie insoluble dans le benzène (1 g.), après plusieurs lavages au benzène, ne fond qu'à 350° C. et est considérée comme truxène.

Remerciements

Nous tenons à remercier Messieurs les Drs. G. S. Whitby et M. Katz pour les précieux conseils qu'ils ont bien voulu nous prodiguer durant l'éxécution de nos travaux. Nos remerciements s'adressent aussi à Monsieur l'abbé Alexandre Vachon, directeur de l'Ecole Supérieure de Chimie, pour l'encouragement qu'il nous a constamment accordé.

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THE SUBSTITUTION OF METHYLENE BLUE THIOCYANATE FOR METHYLENE BLUE CHLORIDE IN THE REDUCTION TEST OF MILK[1]

By H. R. Thornton[2], R. B. Sandin[3] and C. S. Miller[4]

Abstract

Methylene blue thiocyanate has been found to be superior to methylene blue chloride in the reduction test for bacteriological quality of milk, because the thiocyanate is easily prepared in a state of purity approaching 100%.

The widespread use of the methylene blue reduction test on this continent necessitates the frequent duplication of the standard methylene blue chloride tablets certified for this test by the Commission on Standardization of Biological Stains. The reproducibility of a dye involves purification or at least determination of purity. The difficulties encountered in such procedures in the case of methylene blue chloride are serious (1).

At the request of the chairman of the Commission on Standardization of Biological Stains, the authors undertook the present investigation in an attempt to develop improved standards for the methylene blue reduction test. Since it crystallizes readily from aqueous solution without water of crystallization, methylene blue thiocyanate seemed to offer possibilities as a substitute for methylene blue chloride in this test.

Preparation and Analysis of Methylene Blue Thiocyanate

The exhaustive and excellent work of Clark, Cohen and Gibbs (1) has shown that methylene blue chloride is difficult to purify. Various samples prepared by these workers contained excess chlorine and excess sulphur, and gave evidence of small percentages of electromotively active impurities. Drying was found to destroy progressively the characteristic properties. They even suspected slight denaturation when desiccation was carried out at low temperatures.

The work of Drew and Head (4) indicates that methylene blue thiocyanate might have some properties superior to those of the chloride. They report that "Methylene-blue thiocyanate was obtained from the chloride and KCNS in lustrous needles which occurred in two forms: (1) golden-brown (Found:

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Contribution from the Departments of Dairying and Chemistry, University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada.

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C, 59.0, 59.0; H, 5.35, 5.35. $C_{17}H_{18}N_4S_2$ requires C, 59.6; H, 5.25%); (2) beetle-green (Found: C, 58.95; H, 5.3%). The two forms separated from the same mother-liquor." One important fact is that it crystallizes from aqueous solution readily, apparently with *no water* of crystallization or water of constitution. Such is not the case with the methylene blue chloride, some of the purest samples of which are only 89% pure with respect to total dye content. Because of this the thiocyanate seemed to offer possibilities as a substitute for methylene blue chloride in the methylene blue reduction test.

In order to obtain some idea regarding the nature of thiocyanates made from different samples of methylene blue chloride obtained from various manufacturers, a series of thiocyanates was prepared. The thiocyanate in every case was prepared from a hot aqueous, nearly saturated solution of the chloride, which was then filtered while still hot. To the hot filtrate was added a slight excess of pure potassium thiocyanate. On cooling, beautiful crystals of the methylene blue thiocyanate separated. They were filtered by suction, washed thoroughly with cold water, and air dried at 50° C. In a few cases crystallization from hot water was carried out three or more times. A sufficient number of data have not yet been accumulated to indicate the extent of purification that can be accomplished by repeated crystallization.

Analysis of the various products was carried out by means of a titanous chloride titration, which gave the total dye content. The titanous salt solution was made from the 15% aqueous solution and diluted to approximately 0.05 *N*. It was stored in an apparatus similar to that of Thornton and Chapman (8) and preserved under hydrogen. It was standardized twice daily against *pure* ferrous ammonium sulphate, which had been oxidized by *N*/50 potassium permanganate. The actual titration was carried out in a 250 cc. Erlenmeyer flask fitted with a three-hole rubber stopper. One hole was for the tip of the burette and the remaining two were for the entrance and exit of nitrogen gas, which was passed through the solution during the titration. The nitrogen used was tank nitrogen supplied by the Ohio Chemical Company It was thoroughly freed from oxygen by passing it through alkaline pyrogallate and then through 50 cm. of reduced copper gauze contained in a Pyrex tube which was heated electrically.

Table I gives some of the data obtained by the foregoing analytical procedure. The results are the average of two or more closely agreeing determinations.

TABLE I

COMPARATIVE TOTAL DYE CONTENTS OF SAMPLES OF METHYLENE BLUE CHLORIDE AND METHYLENE BLUE THIOCYANATE

Sample	1	2	3	4	5	6	7
Total dye content							
as the chloride, %	87	87.2	80.3	79.9	85.5	59.3	87.5
as the thiocyanate, %	99.7	101.3	101.1	100.6	100.1	99.5	99.8

An inspection of this table indicates the feasibility of converting a chloride of low dye content to a thiocyanate of virtually 100% total dye content.

It must be noted here that an analysis such as that described will not necessarily indicate the presence of small quantities of undermethylated products. For that reason the absorption curves of some of the methylene blue thiocyanates were determined by the Hilger-Nutting spectrophotometer. Undermethylated products can be determined readily with this instrument.

The measurements were made with a standard Hilger wave-length spectrometer provided with a Nutting photometer. The light source was a d.-c. Pointolite lamp. The solutions of methylene blue thiocyanate used were made by diluting an aqueous 0.02% solution 40 times with water. The concentration of the solution is important, since Holmes (5) has shown that in the case of a dye such as methylene blue chloride, the absorption changes with the concentration. Readings were taken using a 2 cm. layer.

Conn (3, p. 64) gives the absorption maximum of methylene blue chloride, if pure, as about 667. Holmes and Peterson (6) have shown definitely that absorption ratios[*] will enable the analyst to identify dyes conveniently and afford information respecting their purity. These workers show that for methylene blue chloride the absorption ratio is 0.59. It would be expected that in the case of the thiocyanate the absorption curve, the maximum and the absorption ratio would be similar to, if not identical with, those of the chloride. Such is the case and a typical absorption curve of a thiocyanate is shown in Fig. 1. The absorption maximum is about 661 and the absorption ratio is 0 61.

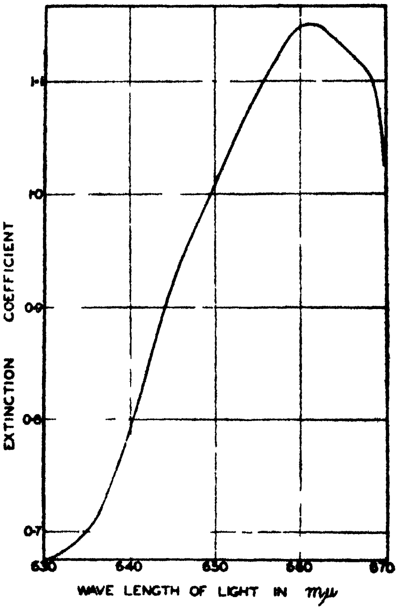

FIG. 1. *Absorption curve of methylene blue thiocyanate.*

Reduction Times in Milk

The methylene blue chloride used in the reduction test technique was in the standard tablet form, and Standard Methods of Milk Analysis (A.P.H.A., 1929) was followed. One part of methylene blue thiocyanate was added to 666,666 parts of milk, giving a depth of blue approximating that observed in the standard test. In each case a modified technique supplemented the standard test. This modification—the tubes were shaken hourly during incubation—tends to eliminate gross variations in the reduction times of replicate samples (9). The reduction times are reported in hours and minutes —thus 6:15 means 6 hr. and 15 min. It is probable that the reading of such color tests is frequently not accurate to within 15 min., especially in the analysis of the higher grade milks.

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[*] *The term absorption ratio is the ratio of the extinction coefficients at two specific wave-lengths, viz., 635 mμ and 665 mμ for methylene blue chloride.*

TABLE II

COMPARATIVE REDUCTION TIMES OF METHYLENE BLUE CHLORIDE AND METHYLENE BLUE THIOCYANATE IN MILK

Milk No.	Standard		Modified	
	Chloride	Thio-cyanate	Chloride	Thio-cyanate
1	6:15	6:05	4:30	4:30
*2	7:05	7:04	5:30	5:30
3	7:15	7:15	4:45	4:45
4	7:15	6:15	4:30	4:30
5	7:45	7:15	6:00	5:55
6	7:45	7:15	5:45	5:45
7	7:45	7:45	5:00	5:00
8	8:00	7:55	6:45	6:45
9	8:00	8:00	6:45	6:45
10	9:15	9:45	7:30	7:20
11	9:30	9:15	7:00	7:00
*12	9:57	9:23	6:30	6:30
Average	7:59	7:46	5:53	5:51

**Average for five determinations.*

The standard reduction times for the 12 milks listed in Table II show an average difference of 13 min. between the reduction time of the chloride and that of the thiocyanate. This is within the experimental error for this grade of milk, which statement is confirmed by the average difference of two minutes when the modified technique was employed. These data show that in this concentration methylene blue thiocyanate may be substituted for the present methylene blue chloride with no resultant changes in reduction times.

Oxidation-Reduction Potentials in Milk

The fact that in the same approximate concentrations in milk, methylene blue thiocyanate and methylene blue chloride reduction times are identical suggests that,

(*a*) The oxidation-reduction potential range over which the thiocyanate is reduced in milk closely approximates that over which reduction of the chloride is effected.

(*b*) The poising effects of the two dyes are not essentially different.

(*c*) Their lethal actions are similar.

So little is known of the lethal effect of methylene blue chloride in milk that it is at present impossible to compare the antiseptic or disinfectant properties of the two salts. Increased concentration of either results in a lengthening of the reduction time, and it is believed that this is due partly to lethal and color effects and partly to poising.

For the measurement of oxidation-reduction potentials in milk the usual apparatus, which included a Leeds and Northrup Type K2 potentiometer, a saturated calomel half-cell and platinum electrodes, was employed. Potentials in milk were measured at a temperature of 37° C. ± 0.5°. Time-potential curves, shown in Fig. 2, represent the potentials set up at electrodes in two tubes of the same milk, one containing methylene blue chloride in the standard concentration, and the other, methylene blue thiocyanate in a concentration of 1 : 300,000. Despite this high concentration of the thiocyanate the poising effect was no greater than that of the standard dye.

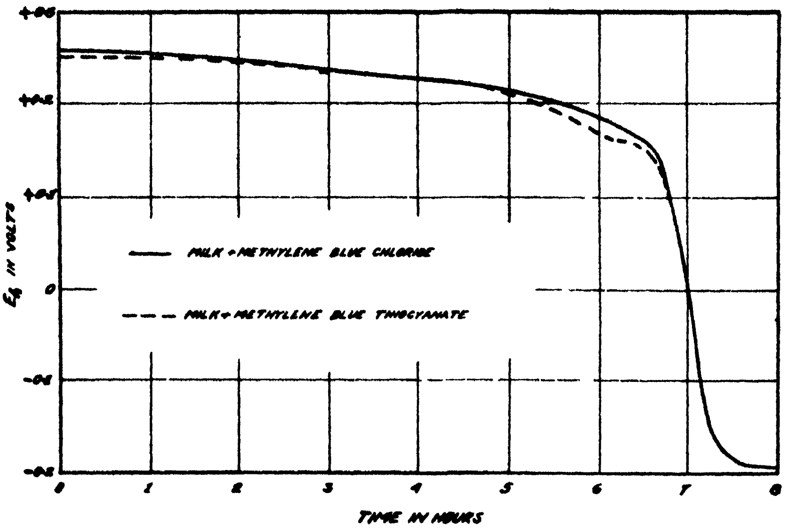

FIG. 2. *Time-potential curves of methylene blue chloride and methylene blue thiocyanate in milk.*

Because the potentials set up at an electrode immersed in a tube of milk are frequently not representative for the entire contents of the tube, it was impossible to determine with accuracy the potential range over which reduction took place in milk. All observations pointed to the reduction of thiocyanate over the same approximate range as that of the chloride.

Oxidation-Reduction Potentials in Aqueous Solutions

A study of the oxidation-reduction potentials of methylene blue thiocyanate in aqueous solutions was also of importance. This work was carried out with the standard equipment already described in the section on oxidation-reduction potentials in milk. It should be mentioned here that a high degree of accuracy, such as that obtained by previous workers (1) with chloride systems, is not claimed.

Potentials in aqueous systems were determined by a titanous chloride titration of 0.0002 *M* thiocyanate solutions, taking all the precautions already mentioned. To keep the pH as constant as possible, the acidity of the titanous salt solution was determined, and then sufficient 0.5 *M* hydrochloric acid was added to a known amount of the dye solution to make a solution of exactly the same acidity as that of the titanous salt solution. However, this procedure does not necessarily ensure a constant pH, but it is believed by the authors that for this work it is sufficiently accurate. Again, the reader's attention is called to previous work in this field (1, 2, 7). It is hoped to repeat this work using highly buffered solutions containing known amounts of reductant and oxidant, the reduced solution being obtained by the use of hydrogen and a platinum catalyst.

In Fig. 3 are shown two typical curves representing the titration of 0.0002 *M* solutions of the chloride and thiocyanate, 0.2094 *M* with respect to hydrochloric acid, at 25° C. ± 0.1°. The half-cell was a saturated calomel electrode. From these curves the end point of the titration is determined. In Fig. 4, the per cent reduction for the two solutions is plotted against E_h. The E_h value at 50% reduction gives the E_0 at a pH that is approximately 0.7, as determined by the hydrogen electrode. Both the chloride and thiocyanate give E_0 values that are almost identical, *viz.*, 0.467 volts.

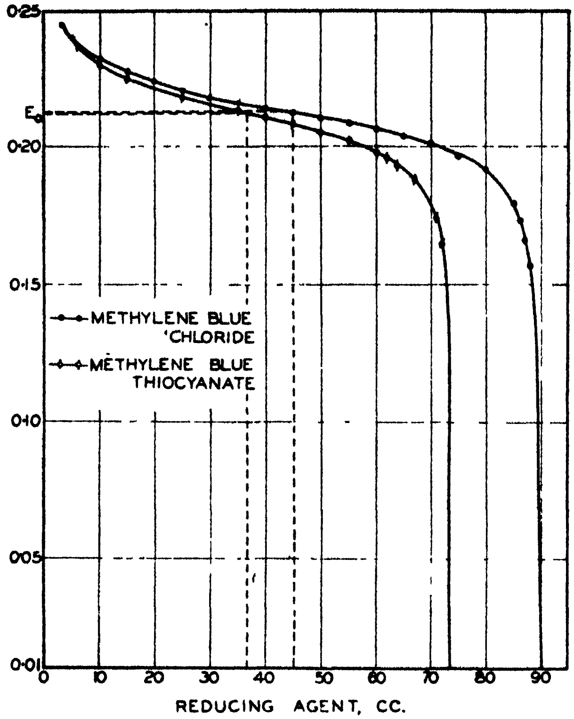

Fig. 3. *Electrometric titration curve for methylene blue chloride and methylene blue thiocyanate.*

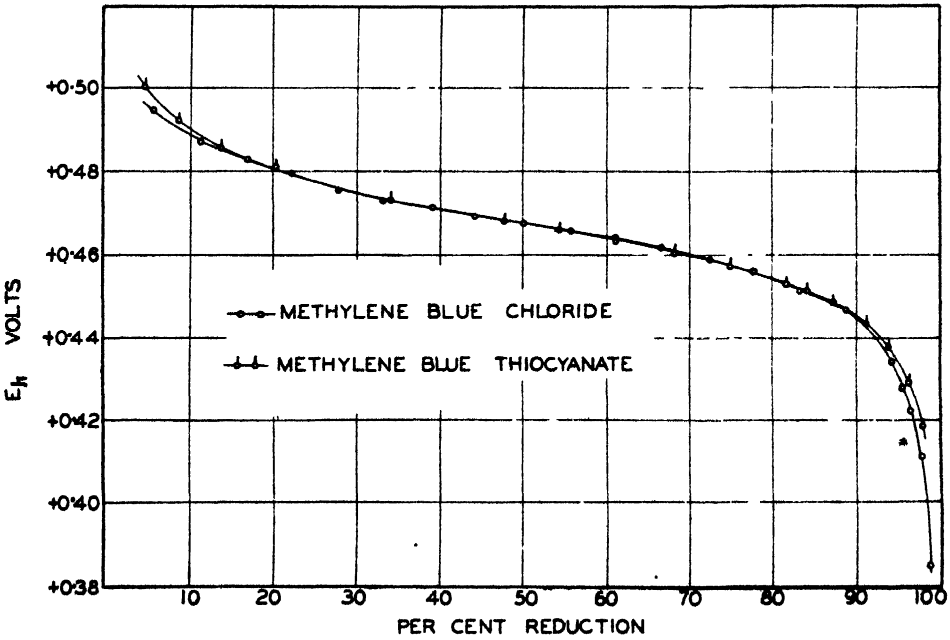

Fig. 4.* *Degree of reduction-potential curves for methylene blue chloride and methylene blue thiocyanate.*

Methylene Blue Thiocyanate as a Stain

Methylene blue thiocyanate has been substituted for methylene blue chloride in the usual staining procedures in a course in general bacteriology without any observed disadvantages. These techniques, however, did not depend upon polychrome properties of the dye. The thiocyanate has been used extensively as a stain in the Breed method of preparing milk smears, and is preferred for this purpose because of the absence of troublesome precipitates. Solubility studies have not been made, but it has been observed by the authors and others that the thiocyanate salt is considerably less soluble in both water and alcohol than is the chloride.

Summary

The standardization of the methylene blue reduction test for bacteriological quality in milk requires the use either of an easily purified dye or one the purity of which is easily determined. Methylene blue thiocyanate is preferable to methylene blue chloride for this test because:—

1. Methylene blue thiocyanate is easily prepared in a state of purity approaching 100%, as shown by titanous chloride titration and spectrophotometric measurements.

2. It reduces over the same oxidation-reduction potential range as the chloride when in aqueous solution and probably when in milk.

3. The poising and lethal effects of the two dyes are not essentially different.

4. When present in approximately equal concentrations, the two dyes have the same reduction times in milk.

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THE NON-PROTEIN NATURE OF A FRACTION OF SOIL ORGANIC NITROGEN[1]

BY A. W. J. DYCK[2] AND R. R. MCKIBBIN[3]

Abstract

It is shown that not all the nitrogen in organic soils is determinable by the Kjeldahl method. In every sample tested the Dumas method gave a considerably higher percentage of nitrogen.

The differences in nitrogen content, as shown by the two methods, vary from 6.4 to 29.6%, hence it is believed that an appreciable fraction of the soil organic nitrogen may be of non-protein nature.

Introduction

Two processes are apparent in the soil: (i) the process of formation of soil organic matter by the decomposition of plant residues and the subsequent accumulation of the decomposition products; (ii) the process of destruction of soil organic matter.

In the process of decomposition of plant residues, the loss of carbon exceeds that of nitrogen, and soil organic matter is considerably higher in nitrogen than the original plant materials. Plants vary widely on different soils qualitatively and quantitatively; their decomposition is brought about by the action of various micro-organisms under different climatic conditions; hence qualitative differences in the composition of soil organic nitrogen compounds may be assumed, *a priori*.

The importance of obtaining knowledge of the forms in which organic nitrogen exists in soils is obvious. It was thought that a comparison between the nitrogen content of soils obtained by the standard Kjeldahl and Dumas methods might be of value, and possibly could point to the nature of the nitrogen compounds in the soils.

Review of Literature

It is believed by many workers that soil organic nitrogen exists largely or totally in the form of proteins. Schmuk* believes that 60–80% of the total nitrogen in the soil belongs to the protein fraction. Remesow and Werigina (3) report that all the nitrogen which is hydrolyzed by hydrochloric acid is of protein nature. They base their conclusions on the analogy of the nitrogen distribution in proteins and the hydrolyzates of chernozem and brown earth soils.

	Amido nitrogen	Mono-amino nitrogen	Diamino nitrogen
"Protein"	9	67.32	25.2
Soil hydrolyzate	9.6	66.9	23.4

Laterite soils according to Remesow and Werigina (3) do not show this analogy.

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**See Reference (3).*

The fact that not all of the nitrogen in soils is hydrolyzed by mineral acids has often been brought forward as an argument that a considerable fraction of this nitrogen is of non-protein nature, but is present in the form of ring nitrogen compounds.

Waksman and Iyer (6) prepared artificial humus from casein and lignin, and compared the extent of hydrolysis of these preparations with that of natural humus. Table I shows their results.

TABLE I

	Unhydrolyzed residue	Per cent of protein nitrogen hydrolyzed
Casein	6.8	80.6
Lignin	94 3	3.2
H-ligno-proteinate	89.3	32.9
Ca-ligno-proteinate	80.3	20.2
Humus from peat	83.0	29.9

It may be seen from the table that natural humus is intermediate between H-ligno-proteinate and Ca-ligno-proteinate, and thus behaves in the same manner as the artificial "humus" preparations.

The behavior of artificial humus preparations toward acetyl bromide, according to Waksman and Iyer (6), is analogous to that of natural humus. They found that whereas proteins are completely, and lignin almost completely, dissolved by acetyl bromide, the artificial humus preparations, like natural humus, were attacked only to a limited extent. Their conclusion is that the non-hydrolyzed nitrogen fraction belongs to the proteins bound in some stable lignin complex.

Other workers have recognized the non-protein nature of a part of the soil nitrogen. Snyder and Potter (5) report an "unknown soluble non-protein nitrogen fraction." They estimated the amount of this fraction as 96–99% of the total nitrogen extractable by a 1% solution of hydrochloric acid. Dragunow (1), working on peats, reports complete absence of the diamino nitrogen fraction in the hydrolyzates.

It is well known (2, 4) that the nitrogen in compounds such as pyridine, quinoline, and their derivatives, and in certain compounds where nitrogen is linked to nitrogen, is not accounted for by the Kjeldahl method. It would follow, therefore, that, if such compounds are present in the soil in considerable amounts, the Dumas method for nitrogen determination should give higher results than the Kjeldahl.

Experimental

Materials

The samples analyzed were taken from widely different locations in the province of Quebec.

Methods

Nitrogen determination by the Kjeldahl method. (*a*) To 2-gm. samples of the soil, 7 gm. of a mixture of 5% copper sulphate (pentahydrate) and 95% potassium sulphate was added, and the whole digested with 30 cc. of concentrated sulphuric acid for 2–3 hr. The ammonia was distilled into 0.1 *N* hydrochloric acid solution.

(*b*) In the case of the hydrolyzates, 10 cc. was measured out into a Kjeldahl flask, 7 gm. of a mixture of 5% copper sulphate (pentahydrate) and 95% potassium sulphate, and 25 cc. of concentrated sulphuric acid were added. The whole was digested 2–3 hr., and the ammonia distilled into 0.01 *N* hydrochloric acid solution.

Nitrogen determination by the Dumas method. (*a*) A portion (0.3 gm.) of the finely powdered sample was mixed with 5 gm. powdered cupric oxide and ignited in a Vitreosil tube 36 in. long, the usual precautions being strictly observed.

(*b*) In the case of the hydrolyzates, 2 cc. of the solution was measured from a microburette into the boat containing the cupric oxide. The combustion was carried out much more slowly, as a disproportionate amount of steam was being evolved.

Blank determinations on 0.3 gm. of sucrose gave 0.15 cc. nitrogen gas. This value was subtracted from the volume of nitrogen collected in each of the above determinations.

Hydrolysis. A portion (100 gm.) of the soil was refluxed for 20 hr. with 500 cc. of 20% hydrochloric acid solution. The mixture was poured into a Büchner funnel and filtered with moderate suction. The first part of the filtrate usually came through turbid and had to be refiltered. The residue was washed five times with 50-cc. portions of hot 20% hydrochloric acid solution, followed by washing five times with 50-cc. portions of boiling distilled water. The filtrate was made up to one litre with distilled water, and the nitrogen determined as shown above.

The non-hydrolyzed fractions were dried in an oven at 100° C. and weighed. They were then ground to a fine powder and the nitrogen determined as shown above.

Results

Tables II and III show the results obtained.

TABLE II

Soil	% nitrogen, Kjeldahl method	% nitrogen, Dumas method	Soil	% nitrogen, Kjeldahl method	% nitrogen, Dumas method
Surface soil muck			*Subsoil muck*		
1	1.28	1.56	13	1.50	1.65
2	1.42	1.98	14	2.40	3.41
3	1.54	1.91	15	1.76	2.00
4	2.47	3.28	16	1.86	2.16
5	1.88	2.01	17	1.89	2.50
6	2.21	2.70	18	2.20	3.12
7	1.91	2.21	19	2.62	3.63
8	2.54	2.78	20	2.15	2.76
9	2.69	2.94	21	1.43	1.62
10	1.63	2.02	22	2.17	2.57
11	1.50	1.82	23	1.83	2.48
12	2.07	2.54	*Raw humus*		
			24	1.47	1.92
			25	1.52	1.86
			26	1.43	1.68

TABLE III

Soil	% nitrogen, Kjeldahl	% nitrogen, Dumas	N_2 expressed as % of total Dumas nitrogen of soil			
			N_2 of hydrolyzate		N_2 of residue	
			Kjeldahl	Dumas	Kjeldahl	Dumas
Surface muck						
1	1.28	1.56	52.37	64.59	26.44	36.73
2	1.42	1.98	50.28	68.40	22.05	31.28
3	1.54	1.91	58.29	73.21	24.53	27.76
Subsoil muck						
13	1.50	1.65	58.17	64.19	28.82	36.36
22	2.17	2.57	57.80	69.39	21.49	30.64
23	1.83	2.48	50.31	63.40	29.60	36.19
Raw humus						
24	1.47	1.92	58.35	80.20	18.46	18.99
25	1.52	1.86	64.40	74.49	14.36	25.16
26	1.43	1.68	65.35	80.12	19.37	19.49

Discussion

The results in Table I show that there are considerable differences in the percentages of nitrogen in organic soils as determined by the Kjeldahl and the Dumas methods. In the soils examined 6.4–29.6% of the total nitrogen is non-determinable by the Kjeldahl method. It is not the authors' intention to attempt to prove or disprove the protein nature of the fraction which is determined by the Kjeldahl method, but it would seem that that fraction which can be determined only by the Dumas method cannot very well be classed in the ordinary sense as "protein" nitrogen, because of its enormous stability toward sulphuric acid digestion. This fraction might exist as ring nitrogen or as nitrogen in the form of some stable compounds in which nitrogen is linked to nitrogen.

The question might occur as to whether Waksman's "ligno-protein complex", which is stable toward mineral acid hydrolysis, may not be responsible for the difference. However, upon inspection of Table III, it will be seen that there is a difference between the nitrogen contents of the hydrolyzates as well as between those of the non-hydrolyzed residues. Furthermore, there are two cases, the raw humus samples numbered 24 and 26, where the nitrogen content of the non-hydrolyzed fraction, determined by the Kjeldahl method, is equal to that of the Dumas method. This appears to exclude the likelihood that Waksman's "ligno-protein complex" is the cause of the difference in nitrogen content shown by the two methods.

It seems obvious that the nitrate nitrogen should have no effect on the difference. In the extreme case, owing to the small amounts present in these soils, it would account for only a negligible fraction of the soil nitrogen. In soils with a carbon content of 0.8% or higher, it is believed that all of the nitrate nitrogen is determined by the ordinary Kjeldahl method. The carbon content of the soils studied far exceeds the 0.8% limit.

From the results it will be seen that the Dumas method gives higher results for nitrogen in the hydrolyzates.

The conclusion of Remesow and Werigina, that the nitrogen compounds in the hydrolyzates are 100% amino acids, is believed to be invalid.

Similarly, the Dumas nitrogen values of the non-hydrolyzed fractions, except in two cases, indicate that this fraction is not, as Waksman and Iyer believe, wholly of protein nature.

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SOME CONSTITUENTS OF THE SAP OF THE SUGAR MAPLE (*ACER SACCHARUM*, MARSH.)[1]

By G. H. Findlay[2] and J. F. Snell[3]

Abstract

Skazin's observation that maple flavor is not present as such in sugar maple sap but develops at boiling temperatures (100–104° C.) has been confirmed. Levorotatory glucosides cannot be detected in sap concentrated to 1/150 its volume, and are therefore probably not present in amounts exceeding 1 gm. (calculated as coniferin) per 50 litres. In maple wood, pyrocatechol tannins were detected but no alcohol-soluble glucosides. The sap contains succinic acid, a glucosidase, an unsaponifiable oil, a water-soluble substance melting at 191.5° C.* and having the composition $C_{11}H_{21}O_9$, and an acetone-soluble substance giving lignin-like color tests. Maple flavor could not be developed in any individual constituent of the sap.

Introduction

Attempts to associate the characteristic flavor of maple syrup and maple sugar with a definite constituent have been only partially successful. Nelson (8) and also Skazin and Snell (14; 15, p. 56) have reported the isolation in minute quantity of an aldehyde resembling vanillin in its odor, and have described some of its properties. They have extracted a larger quantity of an unstable phenolic substance which appeared to be *chiefly* responsible for the flavor. Risi and Bois (10, 11) have expressed the opinion that the aroma is due to a substance of rather saturated nature (less readily oxidized by permanganate than is malic acid), and Labrie (7), working under Risi (12), concluded that the flavoring principle was identical with the material "hadromal," obtained from wood by Czapek (4) and Hoffmeister (6), and associated by the last-mentioned with ferulic aldehyde, the aldehyde of coniferyl alcohol. The standing of hadromal as a chemical compound has not been definitely established (5, 9), though Combes (3) attributed certain histological behavior of lignified tissue to it, and Labrie inferred from odor and absorption spectrum observations that it could be synthesized from vanillin, guaiacol and sucrose (through furfural).

Development of Maple Flavor

It was demonstrated by Skazin (14) that the characteristic flavor of maple syrup and sugar is not present in the sap, but is developed during the boiling. The authors have confirmed this conclusion. The evidence is as follows:

1. Concentration of sap at temperatures lower than the boiling point—*viz.*, by vacuum distillation or by partially freezing out the water and completing the concentration *in vacuo*—produced a syrup with a mild flavor resembling that of watermelons rather than the true maple flavor.

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The experimental results are presented in more detail in a thesis submitted in September, 1934, in conformity with the requirements for the degree of Doctor of Philosophy in McGill University.

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* *All melting points are corrected.*

2. Refluxing at atmospheric pressure developed true maple flavor in the syrup prepared as described above.

3. Heating the vacuum-produced syrup to 105° C. in a sealed tube caused development of true maple flavor.

4. Refluxing of sap at atmospheric pressure, followed by vacuum concentration, produced a syrup of true flavor.

5. Extraction of sap with ethyl acetate followed by concentration of the aqueous layer under atmospheric pressure produced a syrup without maple flavor.

6. Extraction of maple syrup with ethyl acetate did not remove the maple flavor, showing that it must be a precursor of the flavoring principle, and not the principle itself, that dissolves in the acetate.

7. Concentration of maple sap to dryness *in vacuo* yields a yellowish white product of woody flavor. Heated to 100° C. for one to two hours, this product develops a light brown color and the maple flavor.

Search for Glucosides

That the development of the flavor from its precursor is not an oxidation process is evidenced by the fact that as good a flavor can be developed in an atmosphere of carbon dioxide as in the air. In preliminary (unpublished) work in this laboratory, E. E. Massey also produced the flavor by refluxing vacuum-produced syrup in an atmosphere of hydrogen, while heating such syrup with one-tenth its volume of 3% hydrogen peroxide in a sealed tube produced a flavor different from that of maple syrup.

The possibility that the flavoring substance might be liberated from a glucosidic compound by hydrolysis suggested itself. Examination of the data of Bryan (2) revealed no correlation between flavor and invert sugar content. An equal number of syrups of the lowest invert sugar content were classified by him as of "good" and of "mild" flavor, and the same holds true of the syrups of high invert sugar content. Moreover, the one syrup amongst his 481 in which Bryan found no invert sugar was classed as of "fair" flavor. As these estimates of invert sugar were based on reduction of Fehling's solution, no support is afforded for the conjecture that the flavor may be produced by the hydrolysis of a glucoside during the boiling.

However, tests for glucosides by Bourquelot's "biochemical" method (13) were carried out upon fresh sap, sap concentrated *in vacuo* with and without previous freezing, and upon alcohol extracts of the cambium and sap wood of *Acer saccharum*. Bourquelot's test consists essentially in measuring both the polarization and the reducing power of the liquid before and after treatment with invertase and again after treatment with emulsin. If glucosides (levorotatory) are present the emulsin treatment should alter the rotation in the positive sense and also increase the reducing sugar content.

In tests made in the sugaring seasons of 1932 and 1933 on fresh sap and sap concentrated *in vacuo* or by freezing, good agreement was obtained between the observed and calculated changes due to the invertase treatment, indicating that the sucrose was completely hydrolyzed and that the method of determining reducing sugars was reliable. In the emulsin treatment, the 1932 syrups showed slight increases in reducing sugars and positive rotation, but in the 1933 samples changes in rotation varied from −0.14 to +0.1° and in reducing sugars from −0.55 to +0.03 gm. per 100 cc. As duplicate determinations of reducing sugars varied by the equivalent of 1 to 5 mg. of invert sugar, amounting to 0.05 to 0.25 gm. per 100 cc. of sap and 0.1 to 0.5 gm. per 100 cc. of syrup (13.5–30.0% solids), the observed variations are virtually within the limits of experimental error. Furthermore, the observed increases in reducing sugar and in rotation were no greater for the syrups (vacuum or freezing) than for the unconcentrated sap. Even in a concentrate prepared by removal of sucrose from a vacuum syrup by precipitation with alcohol and acetone (see below), the increase of reducing sugar amounted to only 0.20 gm. per 100 cc., and the change in rotation was in the negative direction. The concentration of flavor precursor in this concentrate should be 150 times that in the original sap.

Sap wood and the cambium from the trunk of the maple tree were boiled with alcohol containing a little calcium carbonate, the filtrate evaporated, taken up in water and subjected to treatment with invertase followed by emulsin. Again no evidence of alcohol-soluble glucosides was obtained.

If the development of maple flavor were due to hydrolysis of a glucoside, reducing sugars should be increased in amount by refluxing sap or sap concentrated at lower temperature. The results in Table I, obtained by refluxing for one to three hours, show that no measurable increase occurs.

TABLE I

CHANGES IN REDUCING SUGAR CONTENT OF MAPLE SAPS DURING REFLUX BOILING

Sample	Total solids, %	Invert sugar, gm. per 100 cc.		
		Before refluxing	After refluxing	Change
Sap A	3.5	0.014	0.021	+0.007
Sap B	3.7	0.033	0.027	−0.006
Sap concentrated by freezing	23.0	0.254	0.235	−0.019

It may be calculated from the specific rotations of sucrose and of the glucoside coniferin, which has been regarded as a possible source of maple flavor, that a concentration of 0.3 gm. of the glucoside per 100 cc. would be necessary to yield a conclusive change in optical rotation upon hydrolysis with emulsin. Accordingly, although all the authors' experimental evidence is against the existence of a glucoside in maple sap, the possibility of the presence of such a substance in a concentration lower than 0.002 gm. per 100 cc. (1 gm. in 50 litres) is not excluded.

Extraction of Wood

Freshly cut shavings of the cambium and sap wood of the trunk of a sugar maple cut during the 1933 sugaring season were refluxed 30 min. with the following solvents: water, ethyl acetate, amyl alcohol, petroleum ether. The solutions were concentrated (*in vacuo*, except the petroleum ether extract), any solid sediment filtered out, and the filtrate further concentrated to approximate dryness.

The residues were amorphous except that from petroleum ether, which was very small in quantity (0.01–0.02 gm. per 100 gm. of wood) and melted at 125-130° C. Ethyl alcohol yielded the largest amount of amorphous extract (0.83 and 1.07 gm. per 100 gm. of wood), amyl alcohol the next (0.25 and 0.85 gm.) and ethyl acetate the next (0.25 and 0.30 gm.). No evidence of the presence of coniferin was obtained. The extracts obtained with water and the two alcohols, when taken up in water, responded to Molisch's, Fehling's, Seliwanoff's and Froehde's (molybdic acid) tests. Barfoed's test was also given by the water and ethyl alcohol, and by one of the amyl alcohol, extracts. The petroleum ether and ethyl acetate extracts, however, responded to none of these tests. It may be inferred that the wood contained sucrose and that a monosaccharose was either originally present or produced during the extraction. This monosaccharose yielded glucosazone and must therefore have been glucose, fructose or mannose.

From the water extract, tannins were precipitated by cinchonine sulphate and identified as pyrocatechol derivatives by color and precipitation reactions and by fusion with potassium hydroxide (1).

Vacuum distillation products. In 1933, 8.7 litres of syrup, and in 1934, 13.8 kilos of sugar, were prepared by evaporation of sap at 37–45° C. under reduced pressure. The color of the products was light yellow, the taste sweet and somewhat astringent but not suggestive of maple flavor. Heating the sugar to 100° C. in an oven darkened the color and developed the maple flavor, while neither effect was produced in a parallel experiment with cane sugar. The sugar contained 0.89% of ash, 0.02% of nitrogen and had a pH of 6.1, measured electrometrically in a solution of 20 gm. in 100 cc.

A hydrolytic enzyme. Labrie (7) discovered in maple bark an enzyme ("acerase") capable of hydrolyzing coniferin and amygdalin. He also obtained evidence of an amylase in the sap of the tree.

The authors have found that the addition of tannic acid solution to a solution of vacuum syrup or sugar, but not to ordinary maple syrup nor to refluxed vacuum syrup, results in the gradual development of a purple color. On boiling, a purple coagulum is produced.

With solutions of known enzymes, *viz.*, emulsin, invertase, maltase and trypsin, tannic acid was found to give a light mauve coloration and a precipitate on standing. This color test was given by vacuum sugar, which had been extracted with ethyl acetate, ether or acetone, and also by sugar precipitated from vacuum syrup by alcohol. The substance responsible for the reaction would, therefore, appear to be insoluble in these solvents. It was also removed from aqueous solution by treatment with charcoal or with Lloyd's alkaloidal reagent (hydrated aluminium silicate). No precipitate was given with Millon's reagent, copper sulphate, mercuric chloride (without or with hydrochloric acid) and no color was developed in the biuret test. A positive xanthoproteic reaction was obtained in vacuum syrup, but this was given also by ordinary maple syrup. The enzyme was still present in a solution that had been treated with lead acetate, filtered and freed from lead by addition of sodium carbonate.

One hundred grams of vacuum sugar was ground with 300 cc. of glycerol, allowed to stand 24 hr., centrifuged and decanted. To the glycerol extract, three times the volume of 95% alcohol was added. On standing, 0.048 gm. of flocculent, dirty-white solid (dried *in vacuo* over sulphuric acid) was obtained. This material contained 1.76% of nitrogen and 32.7% of ash. It dispersed in water, forming a turbid mixture which gave the purple color with tannic acid and a purple ring with α-naphthol and sulphuric acid, but no xanthoproteic, glyoxylic or biuret test.

Amygdalin, arbutin, salicin and cane sugar in 0 5% solution incubated at 35° C., with and without addition of a portion of the enzyme, showed no reducing sugar after three days, but at the end of a week the solutions containing the enzyme gave slight Fehling tests while the blanks gave none.

Whether this enzyme is identical with Labrie's "acerase" cannot be definitely stated.

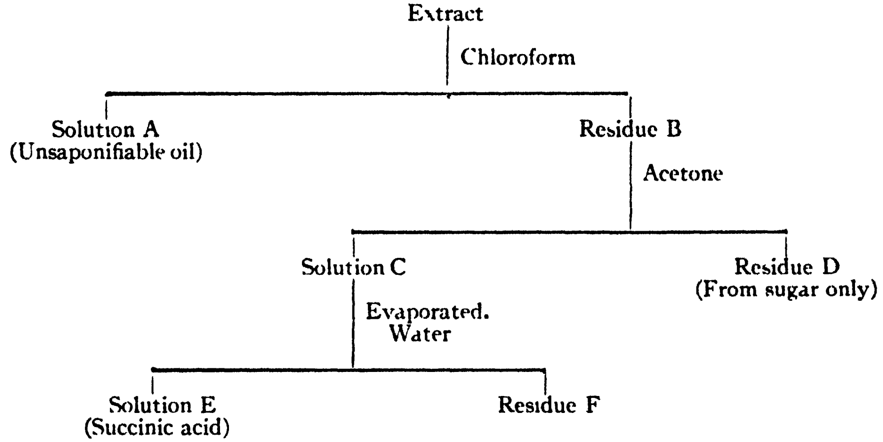
Alcohol-soluble products. It was thought that the flavor precursor might be obtained in more concentrated form by removal of sucrose from vacuum syrup by precipitation with alcohol, or by extraction of vacuum sugar with solvents in which sucrose is insoluble.

1. *Treatment as syrup.* The syrup was further concentrated *in vacuo* to a solids content of about 80% and treated, while still warm, with twice its volume of 95% alcohol, and shaken continually until the sucrose had separated in granular form and then intermittently until cold. The sucrose was filtered off and washed with alcohol. About 80% of the sucrose was thus removed. The alcoholic solution was then evaporated *in vacuo* to a syrup and either (i) extracted with other solvents or (ii) still further evaporated and treated with alcohol or (better) acetone to again reduce the sugar content, and once more concentrated *in vacuo*. The concentrate obtained from 8.7 litres of vacuum syrup after a second precipitation of sucrose amounted to 450 cc. Glucosides, if present, were not in sufficient quantity for detection by Bourquelot's method. Maple flavor could be developed by boiling. Extracts of this concentrate made by shaking it successively with ethyl acetate, ether and amyl alcohol were concentrated by evaporation—*in vacuo* except the ether extract—and treated in the same manner as the extracts of vacuum sugar.

2. *Treatment as sugar.* Fresh sap, 240 litres, of early run and high sugar content (5–6% by refractometer) was distilled to approximate dryness *in vacuo*

at temperatures of 37–45° C. This sugar, of which 13.8 kilos (air-dry) was obtained, was found to yield very little extract to benzene, chloroform or petroleum ether. Acetone dissolved some of the sugar. The best solvents for the non-sugars were ethyl acetate and ether. Extraction with these solvents was carried out in an improvised Soxhlet apparatus capable of handling 500 gm. of solid and one litre of solvent. The extraction was continued for six hours and each portion of solvent was used on four batches of sugar. Four kilograms was extracted with ether, followed by ethyl acetate, and seven kilograms, with ethyl acetate alone. After the ether extract had been concentrated to a volume of 10 cc. it yielded 0.38 gm. of succinic acid and an unsaponifiable oil. The succinic acid melted at 185° C. and its equivalent weight was 56.57 (theory 59). It gave an insoluble silver salt, a red color and—on boiling—a precipitate with ferric chloride, and a white sublimate (anhydride). The unsaponifiable oil remained liquid at 0° C., gave no color reaction with ferric chloride or phloroglucinol–hydrochloric-acid, and had no apparent relation to maple flavor.

The separation of the materials extracted from vacuum syrup and vacuum sugar by ethyl acetate was conducted according to the following flow-sheet.



The oil A resembled that obtained from the ether extract of the sugar, except that it was more viscous and had an acid odor, doubtless due to hydrolysis of the ethyl acetate during concentration. Residue D obtained from the sugar (1934 crop) but not from the syrup (1933 crop), when recrystallized from alcohol, formed colorless, monoclinic prisms, insoluble in ether, slightly soluble in ethyl alcohol and in ethyl acetate, easily soluble in water. Weight 56 mg., m.p. 191.5° C. Found: C, 44.1, 44.1; H, 7.2, 7.1; $OCH_3+OC_2H_5$, 15.1%. Calcd. for $C_{11}H_{21}O_9$: C, 44.4; H, 7.1, OC_2H_5, 15.1 or $(OCH_3)_2$, 16.0%.

The aqueous solution gave no color with ferric chloride, with phloroglucinol–hydrochloric-acid, nor with the Folin-Denis reagent for phenols, no Molisch test and no precipitate with lead acetate. No relation of this substance to maple flavor was observed.

Succinic acid was identified in Solution E by the same tests used with the ether extract, equivalent weights of 58.2 and 58.5 being obtained.

Residue F, a light, yellowish brown powder, was soluble in alcohol, acetone and acetic acid. It also dissolved in dilute ammonia and was reprecipitated upon acidification. It gave color reactions resembling those attributed to lignin, *viz.*, red with phloroglucinol–hydrochloric-acid, orange with benzidine–hydrochloric-acid, yellow with aniline–hydrochloric-acid, deep blue with the Folin-Denis reagent and no color with ferric chloride. The methoxyl values of the residues from the syrup and sugar were discordant, *viz.*, 16.3 and 10.2%.

Although these color tests suggest a relation between maple flavor and lignin (7), it was not found possible to produce maple flavor from this lignin-like material by adding it to dilute sugar solution and boiling to a syrup. On the other hand, no maple flavor could be developed in the extracted sugar by heating it or its solutions. Thus no definite precursor of maple flavor has been isolated in this work, and it would seem possible that, as contended by Labrie, the flavor may be due to interaction of sucrose or a product thereof with other constituents.

Acknowledgments

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THE SOLUBILITY OF LIME IN WATER[1]

By G. L. Larocque[2] and O. Maass[3]

Abstract

The solubility of lime has been determined with a high degree of accuracy over the temperature range 0 to 30° C. by a conductivity method. The degree of dissociation of lime over this temperature range and over the concentration range 0 to 1.164 gm. of calcium oxide per litre has been calculated.

Introduction

As part of the elucidation of the equilibria existing in sulphite cooking liquor (the system calcium-oxide—sulphur-dioxide—water), it was necessary to determine the solubility of lime in water, and the conductivity and degree of dissociation of its saturated solutions. Exact solubility values were also required in lime sorption measurements on cellulose which will be described in a subsequent paper.

Grieve, Gurd and Maass (1) have made a survey of the existing literature and have compared the mean value so obtained with values measured by means of their new conductivity technique, which enables measurements to be made on solutions free from contamination by carbon dioxide. In the present investigation their measurements have been repeated and extended, using their identical method, and values have been obtained for the temperature range 0° to 30° C.

It is characteristic of this method that the solubility values are calculated from conductivity measurements that are virtually unaffected by the presence of colloidal particles, which would seriously affect a gravimetric analysis.

Procedure and Results

In the present work, the apparatus, materials and procedure were the same as those employed by Grieve, Gurd and Maass (1), and are fully described by them.

Solubility Measurements

The method consists essentially in measuring the electrical conductivity, at temperatures from 0° to 30° C., of a series of lime solutions of known concentration, and of a solution having an excess of lime present. These results are given in Tables I and II.

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TABLE I

SPECIFIC CONDUCTIVITY MEASUREMENTS

Conc'n., 0.124		Conc'n., 0 564		Conc'n., 0.724		Conc'n., 0.842		Conc'n., 1.164	
Temp., °C.	*k*	Temp., °C.	*k*	Temp., °C.	*k*	Temp., °C.	*k*	Temp., °C.	*k*
0 10	5.05	0.06	25.08	0 01	29 82	0 10	36.67	0.15	48.41
4 60	5.77	6.16	29.34	8.43	38.72	4.55	40.84	6.15	55.54
10 23	6.78	11.65	33 08	15 47	45.03	9.55	45.80	10 50	62.08
15 42	7.42	20.29	39.19	22 54	51.18	15.55	51.81	17.28	69.90
22 35	8 49	23 01	41.14	31 04	58.72	22.01	58.15	21.78	75.58
29.15	9 51	24 73	42.41			30.10	66.34	29.04	85.15
		30 00	45.97						

NOTE:— *The concentrations are expressed in grams of calcium oxide per 1000 gm. of water and the specific conductivities in reciprocal ohms* $\times 10^4$.

TABLE II

CONDUCTIVITY OF SATURATED LIME SOLUTIONS

Saturated solution: equilibrium values		Saturated solution: temperature falling		Saturated solution: temperature rising	
Temp., °C.	*k*	Temp., °C.	*k*	Temp., °C.	*k*
0 10	57.40	6 42	65 59	8.17	69.43
14 15	73 83	7 12	66 51	8.99	70.26
29 12	89.79	7 65	65 97	12.53	74.63
29 26	89 80	13 80	73 72	18.50	80.89
30 65	90.19	14 28	73 60	19.81	81.84
		25 28	85 45	28.35	89.22

The measurements were carried out in a completely glass-enclosed system, free from air and carbon dioxide. From the conductivity values, isothermal curves, conductivity *versus* concentration for temperatures differing by 5° at intervals from 0° to 30°, were plotted. The concentration of the saturated solution for various temperatures was then determined by extrapolating each temperature curve until it cut a line drawn parallel to the concentration axis, and through the conductivity value of the saturated solution at that temperature. The solubility values obtained in this manner are given in Table III, together with the values obtained by Grieve, Gurd and Maass (1).

TABLE III

SOLUBILITY OF CALCIUM HYDROXIDE IN WATER (EXPRESSED AS GRAMS OF CALCIUM OXIDE PER LITRE)

Temp., ° C.	0	5	10	15	18	20	25	30
Calcd. values	1.456	1.430	1 404	1.370	—	1.333	1.284	1.230
Grieve, Gurd and Maass's values	1.55	—	1 45	—	1.34	—	1.25	—

In the case of the saturated solutions, the equilibrium between the solid calcium hydroxide and the aqueous phase at any fixed temperature is established very slowly, and this likely has been a common source of error in earlier determinations. For this reason, conductivity measurements have been made with rising and falling temperatures, the temperature being allowed to remain constant for 10 or 15 min. before the reading was taken. The results are given in Table II and are plotted in Fig. 1. The magnitude of the observed conductivity value is dependent on whether the equilibrium is reached when the temperature is rising or when it is falling, a final steady value being obtained only at the end of 6 to 12 hr.

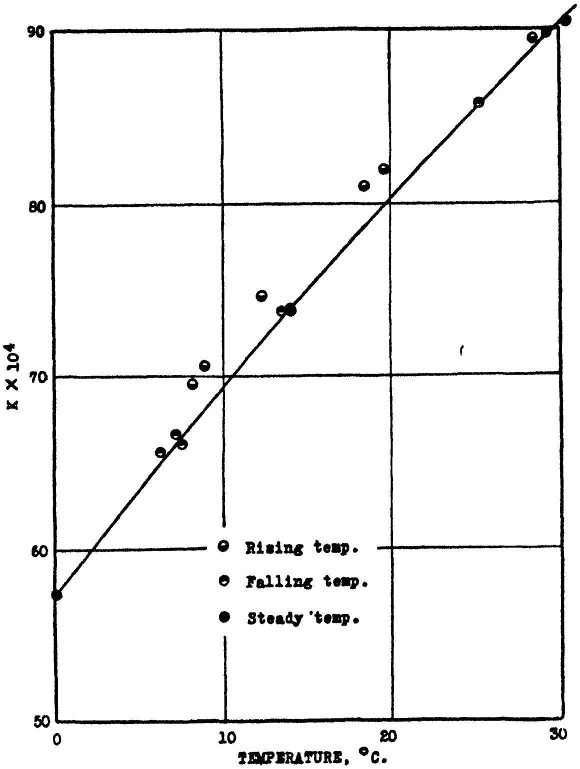

FIG 1. *Conductivity measurements of a saturated lime solution.*

In the case of those measurements made with a rising temperature, the tendency for supersaturation to occur in the system seemed to be greater than that for unsaturation when the final state was reached with a falling temperature.

Degree of Dissociation

It was of interest to determine the extent of the dissociation of the calcium hydroxide at different concentrations and temperatures. The conductivity measurements obtained with each of the five solutions used were plotted against temperature, and from these curves the conductivities at 0, 10, 20 and 30° C. were found by interpolation. The concentration of the ionized calcium hydroxide present at each concentration and temperature was then calculated from the specific conductivity, *k*, and the ionic mobilities of the Ca^{++} and OH^- ions by means of the relation

$$1000\,K = [Ca^{++}]u + [OH^-]v.$$

The concentration of the ionized calcium hydroxide having been calculated, the degree of ionization was then determined from the solubility values. The results are given in Table IV. It is to be observed that the degree of dissociation increases regularly with decrease in concentration and decrease in temperature.

TABLE IV

THE PER CENT DISSOCIATION AND HYDROXYL ION CONCENTRATION (IN GRAM IONS PER LITRE) OF CALCIUM HYDROXIDE AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Conc'n., gm. CaO/litre	0.1024		0 564		0.724		0 842		1.164	
Temp., °C.	[OH⁻]	%	[OH⁻]	%	[OH⁻]	%	[OH⁻]	%	[OH⁻]	%
0	0.0068	94	0 0344	86	0 0430	83	0 0500	83	0.0660	79.3
10	.0070	96	.0336	84	.0426	83	.0487	81	.0644	77.4
20	.0070	96	.0333	83	.0420	81	0481	80	.0628	75.5
30	0069	95	.0330	83	0417	81	.0476	79	.0626	75.3

Grieve, Gurd and Maass (1), in their determination of the solubility, used two reference solutions of concentration 0.536 and 0.737 gm. of calcium oxide per litre, and extrapolated the conductivity values obtained to correspond to a saturated concentration of about 1.40. This extrapolation is too great to give values of sufficient accuracy for an investigation on the adsorption of lime which will be published in a subsequent paper. It was for this reason that the solubilities were redetermined by the authors.

In the present investigation, five solutions of concentration 0.1024, 0.564, 0.724, 0.842 and 1.164 were used, and, as a result, the solubility values obtained are considered to be correct to 0.008 gm. of calcium oxide per 1000 gm. of water over the temperature range 0 to 25° C. The order of accuracy is less for the degree of dissociation values, since the magnitude of the calcium ion mobility is known only to two significant figures.

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THE HEATS OF SOLUTION AND SPECIFIC HEATS OF RHOMBIC SULPHUR IN CARBON DISULPHIDE: THE SURFACE ENERGY OF SOLID RHOMBIC SULPHUR[1]

By A. R. Williams[2], F. M. G. Johnson[3] and O. Maass[4]

Abstract

The heats of solution of rhombic sulphur in carbon disulphide were measured over the concentration range 6 to 17% of sulphur and at 20° and 25° C., and the specific heats of these solutions were calculated. The apparatus designed for these measurements is described. By measuring the heat of solution of finely divided sulphur and its particle size, the surface energy of solid rhombic sulphur is estimated.

Introduction

Since the surface of a solid is so rigid that no appreciable movement towards minimum surface can occur, the measurement of the surface energy of a solid presents a problem altogether different from that involved in the measurement of the surface energy of a liquid. In the hypothesis that the surface energy of a solid is directly proportional to the surface of the solid, a way lies open to the solution of this problem. Thus, if a very large solid surface is produced by finely dividing a material, a measurable amount of surface energy will be produced in connection with this large surface. It is known that the surface energy so produced will manifest itself in various ways, such as in the increased vapor pressure or solubility of small particles or in the increase in the heat of solution of the finely divided solid. Centnerszwer and Krustinsons (7, 8) have attempted to measure this increase in vapor pressure of small solid particles over that of large solid particles and so calculate the surface energy of the solid. Dundon and Mack (9) have calculated the surface energy at the solid-liquid interface of some sparingly soluble solids from a measurement of the increased solubility of fine particles.

Bruzs (6) has attempted to measure the surface energy of a solid as the difference in the heats of reaction when one of the products of the reaction is produced in a finely divided state, and in the other case in a coarsely divided state.

Lipsett, Johnson and Maass (13, 14, 15) have obtained a value for the surface energy of a solid by measuring the difference between the heat of solution of coarsely crystalline, and that of finely divided, material.

Other investigators who have contributed something to the solution of the problem of the measurement of the surface energy of a solid are Jones (12), Hulett (11), Berggren (3) and Born and Stern (5).

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[2] *Holder of a studentship under the National Research Council at the time the research was carried out.*

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[4] *Macdonald Professor of Physical Chemistry, McGill University.*

Experimental

In the present research an attempt is made to measure the surface energy of the solid element sulphur. The method used is essentially the same as that first employed by Lipsett, Johnson and Maass in the measurement of the surface energy of sodium chloride. By this method the energy associated with the surface of a finely divided solid appears as a positive quantity in the difference between the heat of solution of very finely divided material and the heat of solution of coarsely crystalline material. From this difference in the heat of solution and from the measured difference in the areas of the coarse and the fine material, a simple arithmetical calculation gives the surface energy of the solid per unit area.

This difference in the heat of solution for the amount of solid surface produced is rather small, so that the heat of solution measurements have to be made very accurately. To obtain the required accuracy in the present research, an adiabatic calorimeter was used. The calorimeter is of the type described by Lipsett, Johnson and Maass and shown in Fig. 1. It consists essentially of a small inner calorimeter, *A*, air-jacketed by means of a copper cylinder, *B*, and placed in a water bath. A 20 mm. air space insulates the calorimeter from the wall of the copper jacket. Within this small calorimeter, *A*, solute and solvent are placed in such a manner that when the calorimeter is rotated,* the solute and solvent mix and solution takes place. During solution the outer bath is kept at the same temperature as the inner calorimeter, *A*. Thus when the temperature of the inner calorimeter is changing, owing to solution taking place, the temperature of the outer bath is made to change a corresponding amount.

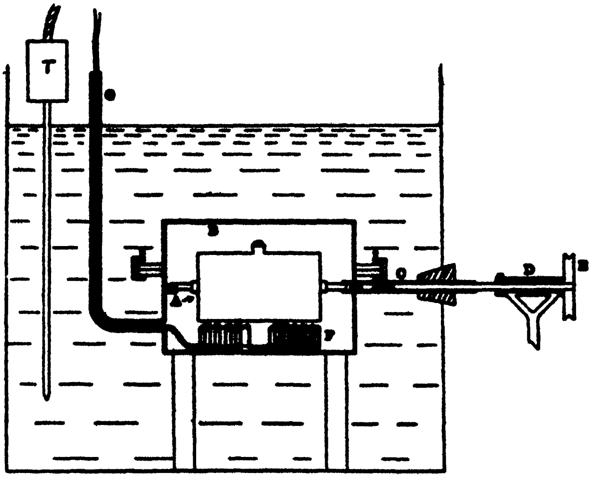

FIG. 1. *Adiabatic rotating calorimeter.*

In order to follow the temperature change of the inner calorimeter with that of the outer bath, the copper jacket is provided with a series of thermoelements, *F*, which record the difference between bath and calorimeter temperature. One set of junctions is blackened and placed about 1 mm. from the surface of the calorimeter, *A*. This set of junctions assumes the temperature of *A* by radiation. The other set of junctions lies along the bottom of the copper jacket, *B*. This set of junctions assumes the temperature of the outer bath by conduction. The thermo-elements are connected to a spot galvanometer. When both sets of junctions are at the same temperature, that is, when the bath and calorimeter are at the same temperature, there will be no deflection of the galvanometer spot. The temperature of the outer bath is controlled by addition of hot or cold water from small taps at the bath surface.

The temperature of the calorimeter is obtained by measuring the temperature of the outer bath. This is possible since by means of the thermo-elements the calorimeter and bath can be brought and kept to within 0.0001° C. of each other while temperature measurements are being made. The outer bath temperature is measured by means of a platinum resistance thermometer, *F*, which records temperatures to within 0.0002° C. Since the total temperature change during a heat of solution experiment is in the neighborhood of 1° C., this temperature-recording apparatus is capable of measuring temperature changes with an accuracy of 0.02%.

In measuring the heat of solution of sulphur it was necessary to use the volatile organic solvent carbon disulphide to dissolve the sulphur. Owing to the corrosive action of sulphur solutions on most metals, it was found necessary to build the small inner calorimeter from "Stabrite" steel, this material being unacted upon by sulphur solutions and in addition possessing the necessary property of good heat conductivity.* New features were required in this calorimeter as compared to the original calorimeter of Lipsett, Johnson and Maass (13, 14, 15), owing to the great volatility of the solvent, carbon disulphide, and also its solvent action on ordinary sealing media such as vaseline or other greases. To render the calorimeter leak proof a satisfactory sealing material was necessary, and this was obtained only after a long investigation.

The calorimeter was so designed that absolutely none of the volatile carbon disulphide could escape either in the liquid or gaseous state, thus eliminating the appreciable error that would arise from the cooling effect of escaping and evaporating carbon disulphide during the course of an experiment. The new features of the calorimeter are brought out in the following description.

The calorimeter is shown in Fig. 2. It is the small calorimeter indicated as *A* in Fig. 1. One end of the calorimeter is removable. This permits introduction and removal of the solute box. This removable end is designed primarily for tightness. Sixteen brass screws press a circular flange into a groove containing a lead gasket. The calorimeter axles are of bakelite, which is a poor heat conductor. Furthermore, bakelite is stronger than glass. The opening which is closed by means of the taper screw shown at the top of the calorimeter serves for the introduction of the solvent after the solute box has been inserted and the removable calorimeter end tightened on. A quantity of solvent sufficient to bring its level halfway to the top of the solute box is introduced.

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* *The calorimeter was machined by Mr. Pye, Technician in charge of the Physics Department machine shop.*

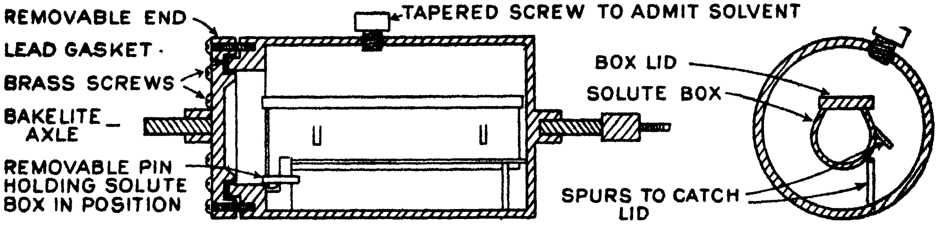

FIG. 2. *Inner calorimeter; A in Fig. 1.*

When the calorimeter is rotated, the solute box becomes inclined and the lid slips from the box opening. The open box containing the solute then dips into the solvent and solution occurs. Rotation of the calorimeter aids in rapid solution. A heating effect caused by the lid tumbling in the rotating calorimeter is eliminated by means of spurs on the side of the box which catch and hold the lid. In order to provide the snug fit that was essential for keeping the solvent vapor from the solute until the proper time for solution, the box lid was ground to the box opening. A sealing medium composed of a mixture of 50% of glucose and 50% of glycerol was used to seal the lid to the box opening. This mixture was insoluble in carbon disulphide, had no action on the sulphur, and its viscosity was such as to allow the lid to slide from the opening when the box was inclined.

To place this small charged calorimeter in position, the top portion of the copper jacket, *B*, Fig. 1, was removed and the calorimeter lowered in. One of the calorimeter axles ends in a small threaded bolt; this bolt screws into the end of a long axle connecting the calorimeter to a motor outside the bath.

The heat capacity of the small inner Stabrite steel calorimeter was carefully determined by measuring the temperature drop when weighed amounts of sodium chloride were dissolved within the calorimeter in weighed amounts of water. From the accurately known value of the heat of solution of sodium chloride in water and from this measured temperature drop, the heat capacity of the calorimeter was obtained with an accuracy of 0.3%.

The sulphur used in the research was Schuchardt's c. p. grade. It was dissolved in pure carbon disulphide and filtered twice through previously extracted filter papers, in order to obtain a perfectly clear solution of sulphur in carbon disulphide. From this solution the rhombic sulphur was recrystallized. In order to remove the last traces of carbon disulphide, the sulphur crystals were broken to the size of pin heads and heated for 24 hr. in an oven kept at 65° C. The purified sulphur was kept in a dark bottle away from light.

The carbon disulphide was a freshly obtained lot of Merck's c.p. grade. To ensure a high degree of purity it was redistilled from ceresine wax after the method of McKelvey and Simpson. The density of this purified carbon disulphide at 25.00° C. was found to be 1.2558 gm. per cc., as compared with 1.2556 gm. per cc. measured by the International Bureau of Physical Chemical Standards as the density of pure carbon disulphide.

Using this pure sulphur and carbon disulphide in the adiabatic calorimeter, the values shown in Table I for the heats of solution of rhombic sulphur in carbon disulphide were measured.

TABLE I

HEATS OF SOLUTION OF RHOMBIC SULPHUR IN CARBON DISULPHIDE

% Sulphur in solution	Heat of solution in calories per mole
Initial temp., 25° C.	
6.30	−405.3
6.30	−405.4
8.00	−404.4
11.73	−403.5
11.73	−403.4
14.19	−403.0
14.19	−403.2
16.56	−402.7
16.56	−402.5
Initial temp., 20° C.	
6.30	398.0
6.30	398.2
8.00	398.0
17.00	395.6
17.00	395.7

In calculating these results three small corrections were necessary. One arose from the cooling effect caused by the evaporation of carbon disulphide into the solute box as the solute box lid was removed, another in determining the heat effect caused by carbon disulphide vapor condensing in the calorimeter as the temperature of the calorimeter dropped owing to solution occurring, and a third was necessary in order to estimate the amount of heat developed due to rotation of the calorimeter. These corrections were all quite small, and in the most unfavorable cases could be summed with an accuracy that would not cause the final experimental result to be in error by more than 0.2%.

The foregoing results are represented graphically in Fig. 3, and they show that the heat of solution of sulphur in carbon disulphide changes only slightly with concentration and temperature. For purposes of comparison the results of previous investigators on the heat of solution of sulphur in carbon disulphide are given in Table II.

TABLE II

HEATS OF SOLUTION OF SULPHUR IN CARBON DISULPHIDE OBTAINED BY OTHER INVESTIGATORS

Observer	Temp., °C.	Concentration	Heat of solution, in cal. per mole
Bellati and Finazzi (2)	0	"Dilute"	−380.3
Bellati and Finazzi (2)	0	Concentrated	−369.6
A. Wigand (18)	0	6.43%	−386.9
A. Wigand (18)	0	8.41%	−396.3
A. Wigand (18)	0	8.74%	−389.2
S. U. Pickering (16)	20	Unstated	−470.4
M. Berthelot (4)	18	Unstated	−410 ± 32

In regard to the accuracy of the values for the heats of solution measured by the authors, it is believed that, from an examination of the data entering into their calculation, they have an absolute accuracy of 0.5% and a relative accuracy of about 0.2%.

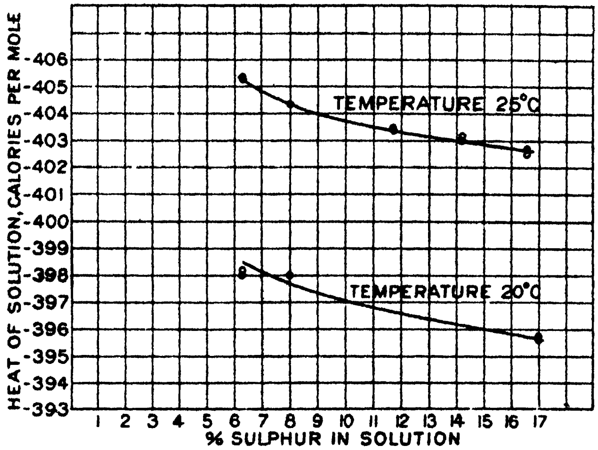

FIG. 3. *Heats of solution of sulphur in carbon disulphide at various concentrations.*

Specific Heat of Carbon-disulphide–Sulphur Solutions

The specific heats of carbon-disulphide–sulphur solutions entered into the calculation of the heats of solution when the total heat capacities of the calorimeter and contents were summed. The only values of specific heats available were those of Marignac, given in the International Critical Tables, and they are of unknown accuracy. It was found possible to calculate accurate values for the specific heat of carbon-disulphide–sulphur solutions by means of the relation

$$\frac{U_2 - U_1}{T_1 - T_2} = C_{Soln} - C_S - C_cS_2 ,$$

where U_2 = Heat of solution of sulphur at temperature T_2.
U_1 = Heat of solution of sulphur at temperature T_1.
C_{Soln} = Heat capacity of the solution.
C_S = Heat capacity of sulphur.
C_cS_2 = Heat capacity of carbon disulphide.

Values calculated for the specific heats of carbon-disulphide–sulphur solutions are shown in Table III.

TABLE III

SPECIFIC HEATS OF SULPHUR–CARBON-DISULPHIDE SOLUTIONS

% Sulphur in soln.	6.30	8.00	11.75	14.19	16.56
Sp. ht. of soln.	0.2373	0.2369	0.2361	0.2355	0.2349

The absolute accuracy of these values rests upon the value for the specific heat or heat capacity of carbon disulphide as used in the calculation. From the results of Regnault (17), Hirn (10), and Batelli (1), the specific heat of carbon disulphide was taken as 0.2389 cal. per gram at 22.5° C. The absolute accuracy of the foregoing specific heat values is probably within 1.0%, while the relative accuracy is within 0.1%.

Heat of Solution of Finely Divided Sulphur

Fine sulphur was prepared by grinding sulphur by means of a mechanically driven agate mortar and pestle. The sulphur was first ground to pass a 400 mesh screen. A preliminary heat of solution experiment was made with this 400 mesh sulphur, in order to discover whether there was a measurable quantity of surface energy associated with sulphur of this degree of fineness. The measurement showed that the heat of solution of this 400 mesh sulphur was 1.2 cal. positively greater than the heat of solution of the coarsely crystalline sulphur. In order to obtain a larger surface and a correspondingly larger surface energy, the 400 mesh sulphur was reground over a period of 12 hr. To insure that this very fine sulphur was not oxidized by the air, a quantity of it was allowed to remain in contact with the air of the laboratory for two weeks and then shaken with distilled water. A very dilute solution of potassium permanganate was added to this suspension of fine sulphur in water, and no decolorizing action was observed upon the potassium permanganate. This was taken to show that there was no solid and unstable suboxide of sulphur present in the finely divided sulphur. Solution of the finely divided sulphur in carbon disulphide also indicated that no amorphous sulphur had been formed in the process of grinding.

TABLE IV

HEATS OF SOLUTION OF FINELY DIVIDED SULPHUR

Temp., °C.	Conc'n of solution, %	Heat of soln., cal per mole
25.00	6.30	−401.2
25.00	6.30	−401.6
	Mean value	−401.4

With this finely divided sulphur the heat of solution measurements shown in Table IV were made.

This value for fine sulphur compares with the value of −405.3 cal. per mole for the heat of solution of coarse crystals of sulphur of the same solution concentration and at the same temperature. The difference between the heat of solution of fine, and that of coarse, particles is 3.9 cal. per mole. This value represents the difference between the total surface energy of coarse crystals and that of very fine crystals of sulphur.

Measurement of Particle Size

For the purpose of estimating the surface energy of solid sulphur per unit area, it was necessary to measure the average particle size of the finely divided sulphur. This was done by taking photomicrographs of the sulphur particles scattered over glass plates. Under the microscope it was seen that the fine particles of sulphur had a marked tendency to cling together. This caused some difficulty in obtaining a clear picture of each individual particle. To scatter and separate the particles, a camel's-hair brush was filled with the fine sulphur and flicked beneath the glass plate, which was held in a gently rising current of air such as occurs near a warm electric light bulb. In another method used to separate the particles, a drop of glycoline was placed on a glass plate and a small amount of fine sulphur introduced into the drop. The drop was smeared over the surface of the glass plate to form a thin film, and photomicrographs were taken of the sulphur particles suspended in this thin layer of glycoline. A Bausch and Lomb metallographic microscope was employed for the work, and two magnifications of 200 and 500 diameters were used. A Brinnel microscope which superimposed an accurate scale graduated in tenths of a millimetre was found useful in reading the particle size from the photomicrographs.

The average diameter of the sulphur particles placed on the glass plate by scattering with a camel's-hair brush was found to be 5μ and 10μ for two different plates. However, even with this procedure, uncertainty arose in differentiating between single particles and aggregates.

The average diameter of the sulphur particle suspended in the layer of glycoline was found to be 5.9μ, 6.1μ and 6.8μ for three different plates in which dispersion was complete. Owing to the better concordance in these latter results their average was taken as the average diameter of the sulphur particle. The diameter of the average particle was calculated using the formula

$$D = \frac{(ad_1^3 + bd_2^3 + cd_3^3 \ldots\ldots)}{ad_1^2 + bd_2^2 + cd_3^2 + \ldots.)} ,$$

where D is the diameter of the "average particle," defined as the diameter of the particle which, if wholly constituting the sulphur, would give the same area per mole as that of the actual particles It may be noted that this hypothetical diameter applies only to a hypothetical number of particles, but that the two may be used in conjunction to calculate correctly both area and volume. a is the number of particles of diameter d_1, b the number of particles of d_2, etc.

Assuming the particles to be spheres (as was indicated by the photomicrographs) and considering the particle diameter to be 6μ, the total surface energy of sulphur per square centimetre could now be calculated.

Area of surface per mole of 6μ sulphur = 160,000 sq. cm.

Surface energy per mole of 6μ sulphur = 3.9 cal.—$3.9 \times 4.2 \times 10^7$ ergs.

$$\text{Total surface energy per sq. cm.} = \frac{3.9 \times 4.2 \times 10^7}{160,000} = 1024 \text{ ergs.}$$

The accuracy of this result for the surface energy of solid sulphur depends upon the value of 3.9 cal. as the difference between the heat of solution of fine sulphur and that of coarse sulphur, and upon the value of 6μ for particle diameter. Owing to the great accuracy that can be obtained with the calorimeter when measuring heats of solution at a definite concentration, the value of 3.9 cal. would be correct to within 10%. There is greater uncertainty however regarding the value for the particle diameter. In the light of the facts that the screen opening was 38μ in diameter and that the sulphur was reground for 12 hr. after passing this screen opening, the value of 6μ would not appear too large. For these reasons it is considered that the value of the particle area is correct to within 30%. Based on this the value of 1024 ergs per sq. cm. for the total surface energy of solid sulphur should be accurate to within about 30%. Even within this accuracy it is of considerable interest to evaluate the surface energy of a non-metallic element such as sulphur.

The question of the influence of an adsorbed layer of gas on the value obtained for the surface energy of a solid is an open one. The authors favor the view that in the case of sulphur it is relatively small. However, experiments are to be carried out in which this factor will be further investigated.

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THE INFLUENCE OF HYDROGEN ION CONCENTRATION WITH PRETREATMENT OF WOOD ON ITS SUBSEQUENT DELIGNIFICATION[1]

By A. J. Corey[2] and O. Maass[3]

Abstract

The results obtained by the authors in a previous investigation have been checked. The influence of an acid, a salt and a base on the pretreatment of wood at 130° C. has been determined. It is shown that pretreatment of wood meal decreases the rate of subsequent delignification. Pretreatment was carried out over the temperature range 100° to 140° C. and the effect of temperature is shown to be very marked. As it was found that the pH of the water after pretreatment decreased, pretreatment was carried out on a chip in which the pH was kept more constant by a forced flow of water through the chip. It is shown that the rate of delignification is increased. Pretreatment was carried out in buffer solutions and it is shown that there is a pH value for which the influence of pretreatment is a minimum. The inferences drawn in connection with sulphite cooking are briefly discussed.

Introduction

In a recent paper (1) the pretreatment of spruce wood chips in water was described. It was found that the heating of the wood chips in water for several hours at 130° C. so changed the nature of the lignin in the wood that the rate of subsequent delignification by calcium bisulphite liquor was greatly retarded. This work has been repeated with a different wood specimen (black spruce). The results previously reported agree as closely as could be expected with the two different samples. The results of this last series are reported in Table I.

TABLE I

Effect of pretreatment of black spruce chips* on rate of delignification

Run no.	Yield of pulp, %	Yield of cellulose, %	Mullen strength, %	Lignin in pulp, %	Residual lignin, %	Length of cook, hr.
A. No pretreatment—cooked at 140° C.						
140	70.0	53.3	—	23.9	16.7	1
139	56.7	49.5	123	12.7	7.2	2
136	52.7	48.5	148	7.96	4.20	3
138	47.3	45.5	134	3.85	1.82	4
137	47.0	46.1	143	2.01	0.94	5
B. Preheated in water for 6 hr. at 130° C.—cooked at 140° C.						
145	74.7	56.6	—	23.1	17.2	1½
141	62.2	51.2	—	17.6	10.9	3
147	56.9	48.5	85	14.7	8.4	4
146	52.8	47.8	99	9.33	4.92	5
144	47.0	44.6	110	4.95	2.33	6
143	42.2	41.0	102	2.99	1.26	7
142	39.7	38.6	95	2.76	1.09	8

* *Density, 0.34; lignin content, 29.9%.*

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[1] *Manuscript received September 18, 1935.*
Contribution from the Division of Physical Chemistry, McGill University, Montreal, Canada.

[2] *Holder of an International Paper Company Scholarship in the Graduate Department of Chemistry, McGill University.*

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An investigation was then made to determine the effect due to the presence of acids, alkalies and salts in the pretreating solution. Wood samples, in the form of chips, were impregnated with water and then heated in various solutions for six hours at 130° C. The chips were removed from the solution and thoroughly washed to remove all traces of the reagent, then dried and cooked according to standard procedure. Two different wood specimens were used. The results of the runs are therefore tabulated in two parts, with a standard cook of each specimen for comparison.

TABLE II

EFFECT OF PRESENCE OF ACIDS, ALKALIES AND SALTS IN THE PRETREATING SOLUTION

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Length of cook, %	Reagent
A. Density of wood, 0.33. Pretreated in neutral salt and alkaline solutions at 130° C. for 6 hr. and cooked at 140° C.						
110	53.2	49.3	7.35	3.9	3	No pretreatment
148	60.7	51.8	14.6	8.85	3	Sat'd. KCl soln.
151	71.3	58.6	17.9	12.7	4	Sat'd. $Ca(OH)_2$ soln.
120	67.5	54.0	20.0	13.6	3	Pretreated in H_2O
B. Density of wood, 0.34. Pretreated in acid and alkaline solutions at 130° C. for 6 hr. and cooked at 140° C.						
138	47.3	45.5	3.85	1.82	4	No pretreatment
149	59.8	51.2	14.4	8.62	4	N/10 acetic acid soln.
150	74.1	47.8	35.5	26.3	4	N/10 NH_4OH soln.

It is seen from Table II, A, that pretreatment of wood in a saturated potassium chloride solution at 130° C. has less effect on the rate of delignification than pretreatment in water. However the subsequent rate of delignification is only one-half that of untreated wood cooked under the same conditions. Heating wood in a saturated solution of calcium hydroxide has a very marked effect on the rate of delignification, as shown in Run 151, in which the time of cooking was one hour longer than that in the others, yet the residual lignin content was nearly as high as that in the pulp obtained in Run 120.

Comparing Run 149, Table II, B, with Run 147 in Table I, B, it is seen that pretreatment of wood in *N*/10 acetic acid solution has about the same effect as pretreatment in water under similar conditions. Pretreatment of wood in *N*/10 ammonium hydroxide solution makes the subsequent delignification extremely difficult, less than 4% of the lignin having been removed from the wood after four hours of cooking.

Since it was shown that the cooking properties of wood are affected by pretreatment in both acid and alkaline solutions, it seemed probable that the effect was due to the hydrogen ion concentration of the solution. When wood is heated in distilled water the solution becomes acidic, owing to the formation of acetic and formic acids. Thus the pretreatment of wood in water really consists of heating wood in an acid solution. In order to determine whether wood structure was an important factor in the pretreatment phenomenon, two samples of wood meal were cooked four hours in bronze bombs of 200 cc. capacity. One sample had been previously heated in water for five hours at 130° C., while the other was untreated. Although the effect was not as striking as that obtained with chips, yet a definite decrease in the rate of delignification was noted in the case of the pretreated wood meal.

TABLE III

THE EFFECT OF PRETREATMENT IN WATER ON WOOD MEAL

Run no.	Yield of pulp, %	Lignin in pulp, %	Residual lignin, %	Condition of wood meal
156A	52 0	4.57	2.37	Pretreated in water
156B	41.8	1.59	.66	Untreated

It is evident that the higher the temperature employed in the pretreatment, the greater will be the quantity of acid formed in the solution. The following series of cooks were made to determine the relation between temperature of pretreatment and the decrease in the rate of delignification. Since the acidity of the solution depends on the temperature, this series also gave an indication of the relation between decreased rate of delignification and the pH of the pretreating solution.

Samples of wood were pretreated in water at 100°, 110°, 120°, 140° C. for six hours, after which they were cooked for three hours at 140° C. pH determinations were made on the cold solutions obtained after the pretreatment.

TABLE IV

WOOD PRETREATED IN WATER AT VARIOUS TEMPERATURES, AND COOKED THREE HOURS AT 140° C.

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Temp. of pretreatment, ° C.	pH of solution
136	52.7	48.5	7.96	4.20	No pretreatment	—
162	48.0	43.5	9.57	4.59	100	4.45
165	53.4	49.1	8.08	4.32	110	4.55
164	58.3	50.1	14.2	8.27	120	4.25
141	62.2	51.2	17.6	10.9	130	—
163	61.2	41.8	31.6	19.4	140	3.42

These results show that there is a close relation between the residual lignin and the pH of the pretreating solution, but they also suggest that the temperature is a very important factor, since only a narrow range of pH has been covered, yet at high temperatures the effect becomes very pronounced. It is well to emphasize here that all pH determinations reported in this paper were made on solutions at room temperature, and thus give only relative values at a higher temperature. Also, when wood is heated in water, the acid is formed within the wood chip and, owing to slow diffusion, the wood is subjected to a higher acidity than an investigation of the solution would indicate. This is clearly shown in the following series of cooks, in which an attempt was made to pretreat wood in a neutral solution. This necessitated the removal of the acid, formed in the chip, at such a rate that the acidity would always be negligible.

In Run 166 the wood chips were placed in the small cooking cell of the penetration apparatus (2, p. 10), and during pretreatment a constant flow of distilled water, about 10 cc. per min., was maintained.

A second attempt consisted of pretreating wood chips in a solution buffered to a pH of 7. McIlvaine's standard buffer solutions were used (3). The pretreatment in Run 169 was carried out in the penetration cell developed in this laboratory (2, p. 9). A cylinder of wood 3½ cm. in diameter and 2 cm. in length was clamped in the cell, and during the pretreatment distilled water was forced under pressure through the chip. The rate of flow was about 10 cc. per min. The centre portion of this chip was used for the cooking experiment, and the results are compared with a run made on the same wood but without pretreatment. The pretreatment in each case consisted in heating the wood in the specified solution for six hours at 130° C., and the wood was then cooked three hours at 140° C.

TABLE V

A COMPARISON OF COOKS MADE UNDER VARIOUS CONDITIONS OF PRETREATMENT

Run no.	Yield of pulp, %	Yield of cellulose, %	Lignin in pulp, %	Residual lignin, %	Conditions of pretreatment
136	52.7	48.5	7.96	4 20	No pretreatment
141	62.2	51.2	17.6	10.9	Heated in water for 6 hr. at 130° C.
166	56.0	48.8	12.9	7.23	Flow of distilled water during pretreatment
168	65.4	56.2	14.01	9.2	Solution buffered to a pH of 7
169	50.3	48.2	4.16	2.09	Forced penetration of distilled water through the chip
6	53.0	51.3	3.32	1.76	No pretreatment

The pretreatment used in Run 166 had little effect on the rate of delignification, compared with normal pretreatment in water, as shown by Run 141. There is an appreciable difference between it and no pretreatment (Run 136). That is easily understood since, although the solution around the chips was changed, the diffusion factor is so great that a marked effect is still obtained. The results of later work, reported in this paper, will explain the significance of Run 168. Run 6 was made under a temperature schedule which differed from that of Run 169 only in that it would correspond to a slightly longer cooking time, so the results are considered to compare fairly closely.

During the pretreatment in Run 169 there must have existed a concentration gradient within the chip, and, since the distilled water used had a pH of about 5 7, the chip must have been heated in the presence of a solution of pH about 4 to 5 as measured at room temperature. This assumption is borne out by later work.

For the next two series of cooks white spruce woodmeal was used. The density was 0 39 and the lignin content 30 9%.

Six samples were sealed in glass bombs filled with buffer solutions of pH ranging from 3 to 8, and heated at 130° C. for six hours. They were then cooked in bronze bombs for three hours at 140° C. The results are tabulated in Table VI, and the curves of lignin in the pulp *versus* pH, and yield of pulp *versus* pH, are shown in Fig. 1.

TABLE VI

SERIES 172. WOODMEAL PRETREATED AT 130° C. FOR SIX HOURS IN SOLUTIONS OF pH 3–8

pH of solution	Yield of pulp, %	Lignin in pulp, %	Residual lignin, %
3	56 0	10 4	5 83
4	53 0	7 4	3 93
5	52 5	7 25	3 81
6	56 0	8 37	4 78
7	58 8	12 6	7 40
8	62 6	14 2	8 89

Series 173 shows the rate of removal of the lignin for a given pH of the pretreating solution. Three samples of woodmeal were pretreated in solutions buffered to a pH of

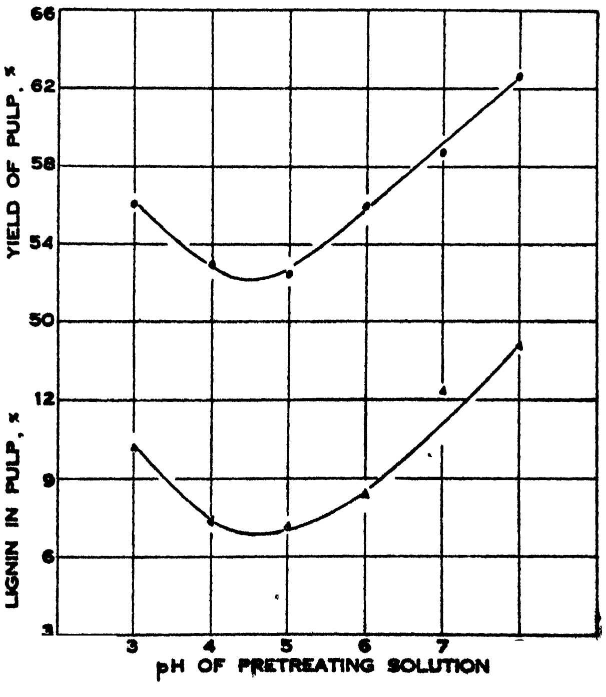

FIG. 1

3, and three in solutions buffered to pH 7. The pretreatment was carried out in glass lined bronze bombs to prevent contamination of the product through the reaction of the solution on the bronze. After periods of two, four and eight hours a bomb from each set was removed. The temperature was maintained at 130° C. After suitable washing and drying the samples were cooked in the glass lined bombs for three hours at 140° C.

Discussion

When the yields of pulp and the lignin in the pulp in Series 172 are plotted against the pH of the pretreating solutions, a minimum is obtained corresponding to a pH between 4 and 5 (Fig. 1) determined on the cold solution. On either side of this minimum the curve rises rapidly, thus explaining the results obtained in Run 168.

From the results of Table VII (Fig. 2) it is seen that for pH below and above 4.6 the length of time of pretreatment increases the difficulty of delignification. At pH 3 the influence of time of heating is as might be expected, approaching a constant value. At pH 7, increased time of pretreatment seems to have an accelerating influence on the difficulty of subsequent delignification. This accounts for the extraordinary influence of ammonia in the pretreating solution.

TABLE VII

SERIES 173. WOODMEAL PRETREATED AT 130° C. FOR TWO, FOUR AND EIGHT HOURS IN SOLUTIONS OF pH 3 AND pH 7

pH of solution	Length of pretreatment, hr.	Yield of pulp, %	Lignin in pulp, %
3	2	47.2	5.3
3	4	53.8	12.7
3	8	58.7	17.2
7	2	54.7	8 46
7	4	55 6	10.8
7	8	63.0	19 2

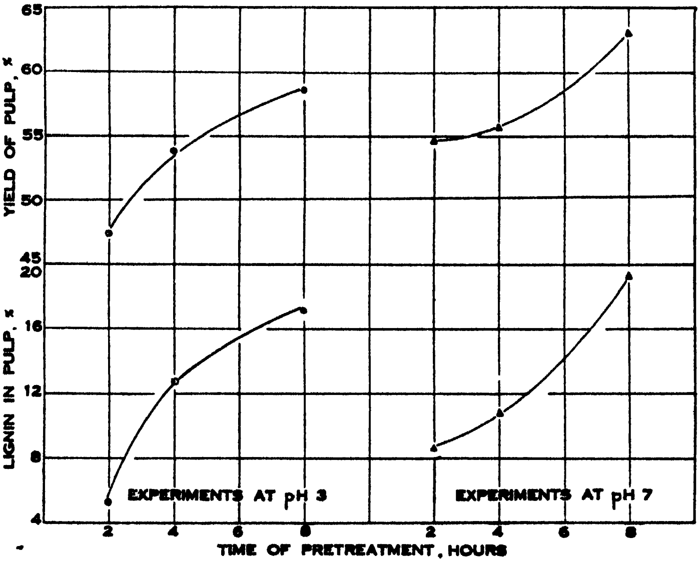

FIG. 2

It cannot be predicted at present in what manner the pH of the buffer solutions will alter with temperature*, but from Fig. 1 it is evident that at a definite hydrogen ion concentration wood may be heated at 130° C. for as long as six hours without any appreciable change in its subsequent cooking properties. Heating the wood in a solution of a higher or lower concentration of hydrogen ion changes it in such a way that it becomes very difficult to delignify by the sulphite process. This is in agreement with the experiment of Klason (4) on the pretreatment of wood meal with hydrogen ion concentration corresponding to a pH of over 7, which greatly retarded subsequent delignification.

The foregoing results are of particular interest in connection with the delignification of wood by sulphite liquor. Work by Gishler and Maass shows that the pH of sulphite liquor at the start of the cook is of the order 3 over a considerable range of concentration, this value being determined at the temperature of the cook. This is lower than the optimum pH that would be deduced from the experiments cited above, and once cooking starts the pH is still further lowered by the formation of sulphonic acids. As was stated above, the optimum pH of 4.6 is that of the buffer solution measured at room temperature, and may in reality be lower. If on further investigation it is found that the optimum pH does not coincide with that of sulphite liquor, it will follow that reduction in cooking time by methods of penetration will be of advantage.

From the results obtained so far it is impossible to deduce with certainty what the influence of hydrogen ion concentration is on the solubilization of lignin, that is, whether a chemical or colloidal change, or a combination of both, takes place. Investigation to clear up this point is under way.

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* *The pH of the solutions used for pretreatment were tested before and after, and it was found that the pH as measured at room temperature was unaltered. The alteration referred to means that, although the pH at 25° C. can be measured at room temperature, there is no telling what it will be at 130° C.*

THE DISCONTINUITY IN THE DIELECTRIC CONSTANT OF LIQUIDS AND THEIR SATURATED VAPORS AT THE CRITICAL TEMPERATURE[1]

By J. Marsden[2] and O. Maass[3]

Abstract

A dielectric cell, which is specially adapted to a study of the dielectric constants of liquid and gas over a large temperature range, including the critical temperature region, is described. The dielectric constants of methyl ether (liquid and saturated vapor) and propylene (liquid and saturated vapor), from room temperature to eight degrees above the critical temperatures, are given. The measurements show that the dielectric constants of liquid and gas are not identical at the critical temperature. These results are in agreement with previous work carried out in this laboratory on the discontinuity in properties of the medium above and below the point of disappearance of the meniscus.

Introduction

In 1902 Eversheim (3, 4) measured the dielectric constant of hydrogen sulphide, liquid and saturated vapor, over a temperature range that extended above the critical temperature of this substance. The data from this research, together with those obtained in its subsequent investigation in 1904, are included in the International Critical Tables (5). Their method of presentation, however, has been altered. Whereas Eversheim plotted his curves in such a way as to indicate that the difference between the dielectric constant of liquid and that of the gas persisted above the critical temperature, care has been taken in the compilation of these data in the International Critical Tables to draw in a curve conforming to the classical idea, that at the critical temperature (disappearance of a visible meniscus) the properties of liquid and saturated vapor become identical.

Experiments in this laboratory (2, 11, 12, 13) have indicated that when a pure liquid is heated somewhat above the critical temperature, even with prolonged stirring, such is not the case.

The actual experimental results of Eversheim seem to be in agreement with the latter point of view. In his later experiments he found that when the condenser was shaken the difference became less marked. It seems difficult to explain why the dielectric constant of the liquid at room temperature should be different, when the liquid was shaken and when it was not shaken, so that it seems possible that the shaking introduced some influence on the measurement of capacity. When the actual experimental results obtained by Eversheim, when the condenser was shaken, are plotted, there is still a marked difference between the dielectric constants above and below the critical temperature.

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada.

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More recently Litvinoff and Litvinoff (7) measured the dielectric constant of liquid ethyl ether over a temperature range including the critical temperature, and found that the dielectric constant of the liquid decreased from a value of 1 796 at 194° C. (critical temperature) to a value of 1.760 at 200° C.

The work in this laboratory showed that if a difference in property existed between the medium above and below the disappearing meniscus, such a difference persisted, provided that there was no measurable temperature difference between top and bottom of the thermostat. Consequently, it was decided to investigate the dielectric constant of propylene and methyl ether, both for liquid and saturated vapor, paying special attention to this precaution.

The pioneer work in this direction was carried out by H. E. Morris (10) in this laboratory. Unfortunately, the repeated failure of the glass, with platinum sealed contacts, prevented the completion of this work. However, results were obtained for propylene, up to within a few degrees of the critical temperature which indicated that an extrapolation of the experimental results would show a marked discontinuity between liquid and saturated vapor at the critical temperature.

The main object of this study was then to investigate the possible persistence of the properties of a liquid above the critical temperature.

Reference to other investigators has been made in previous papers published by this laboratory (2, 11, 12, 13), and there will also be found a discussion regarding their significance.

On account of the unusual experimental difficulties involved, few data are available on the dielectric constant of liquid and saturated vapor, over a temperature range including the critical temperature. At the critical temperature, the dielectric constants of most substances are small, and the pressures involved are very large. Small capacities have therefore to be used.

Experimental

The Dielectric Cell

The first requirement in this investigation was a cell made of glass, in order that the behavior of the meniscus might be observed. This necessitated an electrical contact, made through some type of a glass-metal seal capable of standing pressures as high as 60 atm. Morris (10) found that platinum-glass seals did not withstand the pressures encountered. This difficulty was overcome by the use of frozen mercury seals.

The apparatus is shown diagrammatically in Fig. 1. The condenser bomb, *G*, of specially annealed Pyrex glass, with an internal diameter of 16 mm. and thickness 4–5 mm., was connected by means of capillary tubing to the counterpoise bomb, *H*, of an internal diameter of 13 mm. and thickness 2–3 mm. The condenser, *A*, consisted of a series of concentric brass cylinders, insulated by glass rods and fastened together, so that it could be moved as a unit. The capacity of the condenser was approximately 25 *μμf*.

The condenser was connected to a soft iron counterpoise, *E*, by means of a fine brass wire which served also as a lead for the outer plates of the condenser. Copper wire insulated with cotton was soldered to the lead wire, and passed longitudinally through the centre of the counterpoise, and was soldered in turn to a brass spring, *B*. Another spring, fastened to the bottom of the condenser, served as a lead for the outer plates of the condenser. The springs were sufficiently flexible to permit an unhampered movement of the condenser. The end of each spring was soldered to a nickel wire which made contact with the mercury. The wires were in turn wedged into place in the capillary, so that the springs were kept taut.

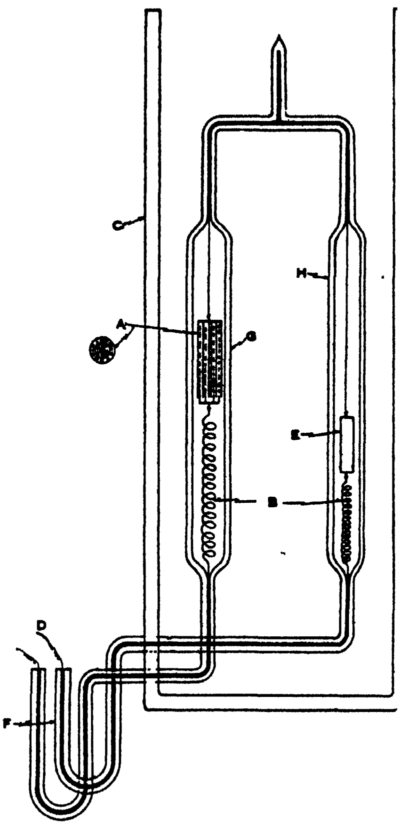

FIG. 1. *Diagram showing the dielectric cell.*

The capillary arms of the cell passed through two holes drilled in the side of a Pyrex jar *C*, where they were fastened securely with litharge-glycerine cement, and each terminated in the form of a U. Mercury was introduced into these U-tubes and frozen with a carbon-dioxide-acetone mixture. Hydrochloric acid was added to the latter, to make it a conducting medium, which could be grounded. Care had to be taken that no air was trapped by the mercury, otherwise on evacuation it would be drawn up into the cell. To prevent this, the mercury seals were filled simultaneously by means of a T-joint connecting the U-tubes to a manometer provided with an attached leveling bulb. After evacuation of the cell, the leveling bulb was raised until the desired amount of mercury was introduced.

Contact between the measuring set up and the dielectric cell was made through two wires, *D*, dipping into the mercury seals.

Measurement of Dielectric Constant

The heterodyne beat method was used for measuring capacity. In the preliminary work carried on by Morris (10), the oscillators were of the Hartley type. This apparatus had one serious disadvantage in that it was affected by stray capacities. This difficulty may be overcome by special operating technique when the experimental cell is placed near the measuring apparatus.

However, in this work the experimental cell had to be placed about eight feet from the measuring apparatus. Stray capacities were also introduced by the metal supports surrounding the bath.

The measuring apparatus finally adopted by Morris (10) and used by the authors is shown in Fig. 2. The Hartley principle was replaced by a tuned plate circuit in which the plates of the variable condensers were grounded; body capacities were thus eliminated. The hook-up consists of two oscillators with a detector and amplification unit. A frequency of 1,000,000 was employed.

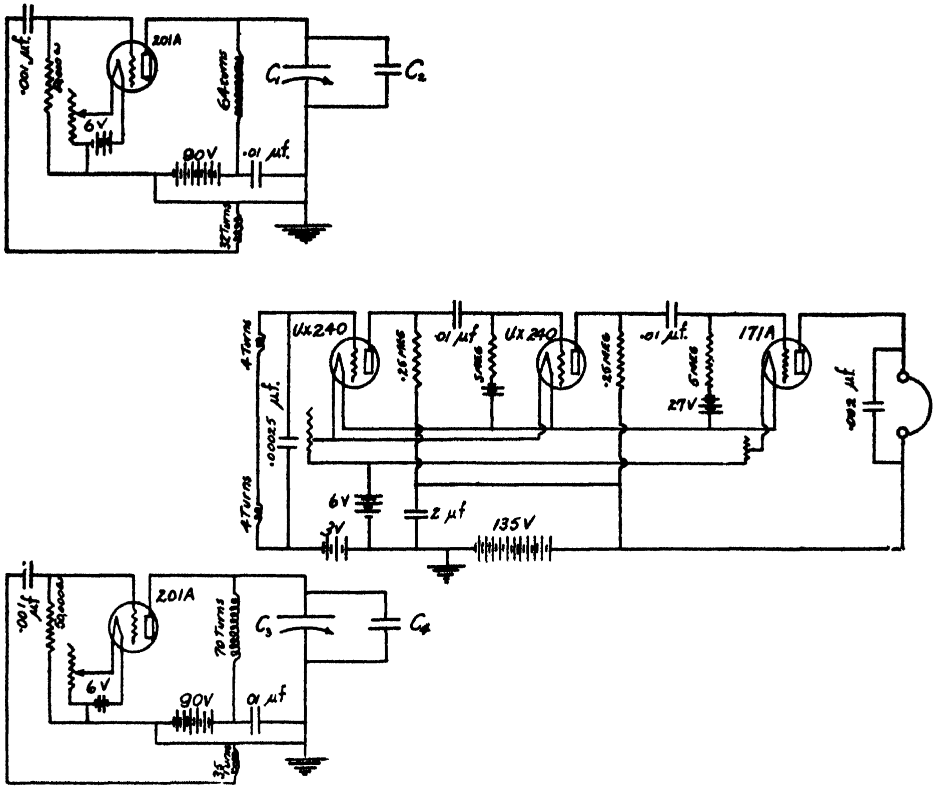

FIG. 2. *Diagram showing oscillators and amplifier.*

Since small changes in capacity were measured, the following method of increasing the accuracy of the readings was used. A mirror, with a vertical cross hair was fastened to the arch of the rotor plates of the condenser. The latter was placed in the centre of a five foot wooden circle, with a vertical millimetre scale around its circumference. A beam of light directed on the mirror and reflected to the scale gave a sharp shadow of the cross hair capable of being read to 0.5 mm. The condenser was adjusted, by means of a pulley attached to the rotor plates, and connected to another pulley placed outside the wooden circle.

The experimental condenser C_2 was placed in parallel with C_1, and could be cut out by means of a mercury switch, thus allowing the lead capacities to be checked after every reading. This switch, placed near the experimental cell, was operated by a system of pulleys at a safe distance from the bath. The oscillators and amplifier were enclosed in galvanized iron boxes. All leads were encased in copper tubing and the latter grounded. A condenser, C_4, was inserted to offset lead capacity.

In operation, the variable condenser, C_3, was adjusted so that a zero sound reading was obtained when the condenser C_1 was set in a position such that it gave a convenient reading on the scale. The experimental cell C_2 was connected in parallel with C_3 and C_1 readjusted. The difference in capacity of C_1 gives the capacity of C_2. The set-up was such as to make the range of inaudibility in the phones small, and the difference between the scale reading at which sound could be heard and that at which it could not be heard was less than 2 mm. In making measurements the zero sound reading was, of course, always approached from the same direction. A change of 0.00192 in dielectric constant corresponded to a change of 1 mm. on the scale. For each dielectric constant determination, the reading for the leads and that for the cell inserted were taken, and the reading for the leads checked. This series of observations was repeated four times at about two-minute intervals. It was found that the scale readings agreed within 1 mm. on the average. The procedure for the calculation of dielectric constant will be shown later.

The Heating Bath

The bath, *C* (Fig. 1), was a three gallon Pyrex jar. Dibutyl phthalate was used as the liquid medium since it does not discolor as rapidly as most bath liquids. It was thus possible to see the meniscus in the bomb.

A steel drum which served the double purpose of a shield for the experimental condenser, and also as a preventive measure in case of an explosion, surrounded the thermostat. Three 200-watt Mazda lamps placed behind holes cut in the drum gave suitable lighting in the thermostat.

The dielectric cell was supported by two adjustable aluminium rings, attached to a steel rod.

Vertical movement of the condenser was effected by means of a solenoid, with an iron core, which controlled the position of the counterpoise. This solenoid was mounted on a carrier running in a grooved brass rod. The carrier was connected by a steel chain which passed over a toothed wheel, mounted on an axle, to a lead counterpoise. A large pulley fixed on this axle and connected by a belt to another pulley about eight feet distant, permitted manipulation of the magnet at a safe distance from the bath.

In a study of this kind, one of the most important factors is temperature control. Not only must the temperature be kept constant, but also a temperature gradient, between top and bottom of the bomb, must be avoided. By means of a telescope, temperatures were read on a standardized thermometer graduated in tenths of a degree. A copper-constantan thermocouple, having four junctions at the bottom and four junctions at the top of the bomb, indicated any temperature difference. The thermocouple was connected to a sensitive D'Arsonval galvanometer. A scale was placed about seven feet from the mirror of the galvanometer. A deflection of 1 cm. on this scale corresponded to a temperature differential of 0 02° C.

Two heaters were placed at the sides of the bath, and one at the top and one at the bottom; the last two were so adjusted as to eliminate any temperature difference shown by the thermocouple. A four bladed stirrer was used. It was found possible to maintain uniformity of temperature in the bath to better than 0 01° C.

A 110 volt d.c. circuit supplying power for heaters, magnet and motor was grounded through a 10,000 ohm resistance. All metal parts surrounding the bath were grounded.

The whole bath assembly was enclosed in a wooden box fitted with safety glass windows.

Preparation for an Experiment

The capillary T-joint at the top of the dielectric cell was connected to a vacuum pump. The cell was heated to 100° C. and alternately evacuated and flushed with air dried over phosphorus pentoxide.

Propylene was prepared, as described by Maass and co-workers (1, 8, 9), by the dehydration of isopropyl alcohol over alumina at 350° C. Purification was carried out by low temperature fractionation, the purity being checked by the vapor pressure after every fractionation.

Methyl ether (99 9%), obtained from Ohio Chemicals, Ltd., was condensed into the fractionation system, and purified in the manner described for propylene.

The cell was evacuated and flushed several times with the substance to be investigated. A volume of liquid equal to 24/85 of the total volume of the cell was distilled in, from a graduated tube, the bath being cooled with a carbon-dioxide–acetone mixture.

C. p. benzene, dried over sodium, was used in the calibration of the condenser.

Results

*Methyl Ether**

The condenser was calibrated with air and benzene. The dielectric constant of liquid methyl ether at two temperatures was then calculated from these data, the temperatures chosen being such that the dielectric constants differed by a large amount. These measurements were made directly, one after the other. Knowing the dielectric constant at these two temperatures, these values could be used in all subsequent experiments for purposes of calibration. This was necessary in view of the fact that there was a slight change in the capacity of the set-up, owing to the rearrangement of the apparatus and to other causes. The foregoing calibration was carried out as follows.

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* *Critical temperature, 126.9° C.*

The dielectric constant of the medium in the condenser cell is C_x, where C_x is the capacity when the medium is substance x and C_a when it is air.

Let C_b = capacity of condenser in benzene
C_m = capacity of condenser in methyl ether
ϵ_b = dielectric constant of benzene
ϵ_m = dielectric constant of methyl ether.

Then

$$C_b = \epsilon_b C_a \tag{1}$$

$$C_m = \epsilon_m C_a . \tag{2}$$

The capacity of the condenser in air is given by

$$L + C_a = kD_a , \tag{3}$$

where L is the capacity of the internal leads, including mercury seals, D_a is the deflection of the experimental condenser in air, as measured on the scale of the precision condenser, and k is the proportionality factor. Similarly

$$L + C_b = kD_b \tag{4}$$

$$L + C_m = kD_m . \tag{5}$$

It follows, by substituting the values of C_b and C_m obtained by means of Equations (1) and (2) in Equations (4) and (5), respectively, that Equations (3), (4) and (5) may be solved simultaneously to give

$$\epsilon_m = \left\{ \frac{(D_m - D_a)(\epsilon_b - 1)}{(D_b - D_a)} \right\} + 1.$$

From this equation the dielectric constant of methyl ether was determined at two temperatures, t_1 and t_2, the deflections being D_{t_1} and D_{t_2}.

From previous equations it follows that,

$$C_a(\epsilon_{t_1} - 1) = k(D_{t_1} - D_a)$$

and

$$C_a(\epsilon_{t_2} - 1) = k(D_{t_2} - D_a).$$

Solving

$$k = \frac{C_a\,(\epsilon_{t_1} - \epsilon_{t_2})}{(D_{t_1} - D_{t_2})}.$$

TABLE I

THE RELATION BETWEEN THE DIELECTRIC CONSTANT OF LIQUID METHYL ETHER AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
24.5	5.034	95.8	3.338	127.6	1.903
37.3	4.732	100.3	3.227	128.2	1 899
50.5	4.424	103.2	3.167	128.3	1.885
55.5	4.310	104.9	3.114	130.4	1.878
60.6	4.179	109.0	2.993	131.7	1.873
66.3	4.048	115.3	2.811	135.6	1.860
69.95	3.949	116.9	2.749		
75.0	3.831	120.6	2.615	*Hysteresis curve*	
80.3	3.712	123.2	2.492		
85.1	3.598	125.0	2.369	130.0	1.874
90.2	3.474	126.1	2.257	127.8	1.882

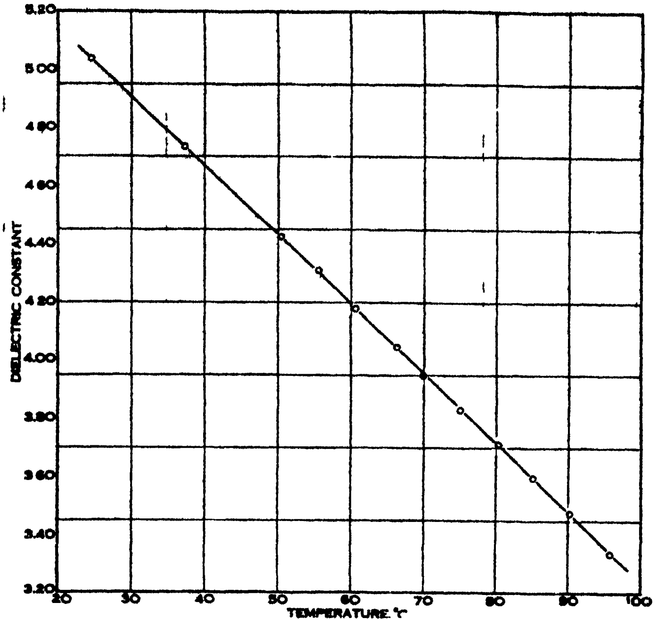

FIG. 3. *The dielectric constant-temperature relation for methyl ether liquid from 25° to 100° C.*

Having determined $k(0\ 0193C_a)$, it was possible to calculate the dielectric constant of methyl ether at any other temperature at which the deflection was measured.

It was convenient to obtain the dielectric constant of the gas above the critical temperature by raising the condenser into the gas phase, and comparing the dielectric constant of the gas with that of the liquid. The reason for this will be discussed later. The dielectric constant of the gas was calculated on the assumption that the dielectric constant of the liquid and that of gas were the same at 135° C., eight degrees above the critical temperature, *i.e.*, 1.860 as determined from the liquid curve. Knowing the change in deflection of the condenser with change in temperature and the dielectric constant at 135° C., the dielectric constant was determined for different temperatures, in the same manner as described for the liquid.

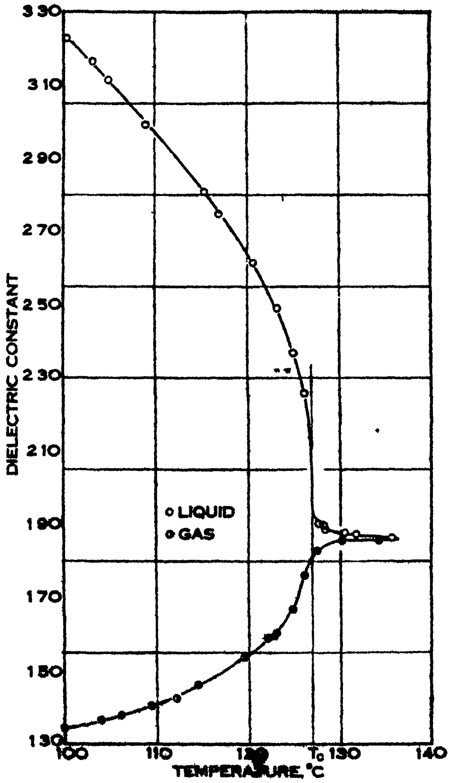

FIG. 4. *The dielectric constant-temperature relation for methyl ether liquid and gas from 100° to 135° C.*

TABLE II

THE RELATION BETWEEN THE DIELECTRIC CONSTANT OF METHYL ETHER GAS AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
59.2	1.225	112.2	1.426	126.0	1.760
80.0	1.262	114.5	1.462	127.4	1.827
100.0	1.343	119.5	1.538	130.1	1.858
104.1	1.364	122.0	1.590	134.1	1.856
106.1	1.377	123.0	1.605		
109.4	1.404	124.8	1.667		

Propylene[*]

The dielectric constants of propylene were calculated from the absolute values of the dielectric constant at 45 and 65° C., as given by Morris (10). The relative changes in deflection with temperature were measured, and the dielectric constants calculated in the same way as described for methyl ether. The value of the proportionality constant, k, is 0.0191 C_a. Incidentally, this is an independent check of the value 0.0193 C_a found in the previous calibration.

TABLE III

RELATION BETWEEN THE DIELECTRIC CONSTANT OF PROPYLENE LIQUID AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
21.0	1.873	65.0	1.690	89.9	1.445
25.1	1.864	67.9	1.669	90.7	1.419
29.9	1.852	71.4	1.654	91.4	1.375
34.5	1.843	75.7	1.625	91.6	1.350
39.2	1.824	81.1	1.579	91.9	1.331
45.0	1.795	83.5	1.547	93.1	1.318
50.2	1.779	87.6	1.493	96.4	1.314
54.8	1.742				

The dielectric constant of the gas was calculated in the same way as described for methyl ether. The dielectric constant of gas and liquid were assumed to be equal at 100° C., eight degrees above the critical temperature.

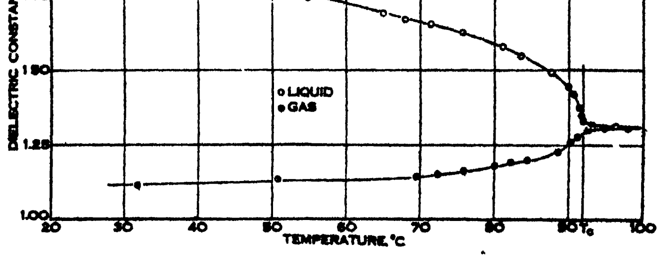

FIG. 5. *The dielectric constant-temperature relation for propylene liquid and gas.*

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[*] *Critical temperature, 91.9° C.*

TABLE IV

RELATION BETWEEN THE DIELECTRIC CONSTANT OF PROPYLENE GAS AND TEMPERATURE

Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant	Temp., °C.	Dielectric constant
31.8	1 114	80.0	1.182	90.2	1.258
50.8	1 134	82 2	1.194	91.1	1.279
69.5	1.144	84.4	1.203	92.6	1.304
72.4	1.151	88.5	1.228	94.8	1.310
75.9	1.165	89.9	1.254	98.0	1.310

Discussion

The cell has been designed in such a way that simultaneous measurements of the dielectric constants of liquid and vapor could be made by moving the condenser, by means of the magnet. This was, of course, of particular interest in connection with determinations above the critical temperature.

Such experiments were carried out with propylene and the results shown in Table V were obtained.

TABLE V

DIELECTRIC CONSTANTS OF PROPYLENE GAS AND LIQUID*
(NOT CORRECTED FOR DISPLACEMENT OF CONDENSER)

Temp., ° C.	°C. above critical	ε liquid	ε gas
91 9	0	1.331	1 226
93.1	1.2	1.318	1.239
96 4	4.5	1.314	1.257

* *As determined by simultaneous measurements on liquid and gas, above the critical temperature. The constants for the gas are based on the absolute values of the liquid, with the assumption that displacement of the condenser cell from its normal position in the liquid caused no change in capacity.*

It will be seen that with rise in temperature the dielectric constants of gas and liquid approach each other, but the difference is far too great when compared with the results of Winkler and Maass (13), and Tapp, Steacie and Maass (12).

It was thought that this might be due to a change in capacity when the condenser system is moved vertically in a uniform medium. This could be accounted for by a relative change in position of the brass spirals during the movement. Consequently measurements were carried out when the condenser arm was filled with benzene. It was found that there was a change in capacity.

This change in capacity can best be presented in terms of an apparent change in the dielectric constant of benzene, for purposes of the calculation of the dielectric constant of the gas. When the condenser was immersed in the liquid propylene (the normal position in the liquid), the accepted value for the dielectric constant of benzene at 59.2° C. of 2.198 is taken (6). When the condenser was moved into the position where, in the propylene medium it was in the gas (normal position in the gas), the apparent dielectric constant of benzene was found to be 2.145. These changes in capacity were found to be reproducible, thus showing definitely that there was a change in capacity when the position of the condenser was changed in the condenser arm filled with a uniform medium, the counterpoise arm being filled with air.

When this correction is applied to the results shown in Table V, the values of the dielectric constant shown in Table VI are obtained.

TABLE VI

DIELECTRIC CONSTANTS OF PROPYLENE GAS AND LIQUID*
(CORRECTED FOR DISPLACEMENT OF CONDENSER)

Temp., °C.	ε liquid	ε gas
91.9	1 331	1.279
93.1	1.318	1 292
96.4	1 314	1.310

* *As determined by simultaneous measurements of liquid and gas above the critical temperature. The constants for the gas are based on the absolute constants of the liquid, but are corrected for the displacement of the condenser cell, the corrections being based on the apparent variation of the dielectric constant of benzene with displacement from the normal position.*

It was decided not to use this method, as the correction is probably not quite sound. This is because of the fact that the medium (propylene or methyl ether) introduced into the cell was of such an amount that some liquid was in the counterpoise arm, since as it has to be arranged that the visible meniscus in the condenser arm would disappear in such a position that the condenser could be moved from below to above the point of disappearance of the meniscus*.

However, these data illustrated the following phenomenon. When the meniscus disappears, a difference in medium persists above and below the point where it was last seen. This difference becomes less with rise in temperature, above the critical. As the bath temperature was kept constant, at each temperature above the critical, during the time when the condenser was moved up and down, these experiments show that the considerable stirring brought about by this movement did not destroy the difference in dielectric constant.

Because of the uncertainty of the correction to be applied for the up and down movement of the condenser, the absolute values for the dielectric constants of the gas were calculated on the assumption that at 8° C. above the critical temperature the medium would be uniform, within the accuracy of measurement.

The data presented are of interest in two ways. The dielectric constant of two liquids and their saturated vapor have been measured, and it has been shown that above the critical temperature a difference in dielectric constant persists between the medium, above and below the disappearing meniscus.

The interest attached to the first will be discussed in a subsequent paper, as it was not the main object of the present investigation, except in so far as to point out the extraordinary difference in the shapes of the methyl ether and the propylene curves (Figs. 4 and 5). The dielectric constant of liquid methyl ether decreases with extraordinary rapidity from one degree below the critical temperature to one degree above, whereas the relatively non-polar propylene shows a far less marked dielectric constant temperature gradient.

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* *It was mentioned before that the space was filled to 24/85 of the total volume of the bomb, in order to have the meniscus disappear at the same position, as it was at room temperature. This was very difficult on account of the large dead space in the counterpoise arm, as well as in the condenser arm. The distribution of liquid between the condenser arm and counterpoise arm was brought about by evaporation and condensation, and by trial and error the relative amounts were so adjusted that the condition mentioned above could be brought about.*

With regard to the second, the following observations may be made. The results are in agreement with the experiments carried out in this laboratory by Maass and co-workers (2, 11, 12, 13) on what happens above the critical temperature. They could of course have been predicted from the fact that a difference in density between gas and liquid persists above the critical temperature, and that on lowering the temperature a separation into the original composition of the medium above and below the disappearing meniscus does not take place*. The data will perhaps be useful when additional data obtained in investigations now in progress on refractive index, viscosity and solubility above the critical temperature have been accumulated.

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* *See hysteresis data in Table I.*

STUDIES IN THE SYSTEM CALCIUM-OXIDE–SULPHUR-DIOXIDE–WATER

II. CALCULATION OF IONIC CONCENTRATIONS[1]

By P. E. Gishler[2] and O. Maass[3]

Abstract

The conductivity and vapor pressure data of the system calcium-oxide–sulphur-dioxide–water presented in an earlier paper have been used to calculate ionic concentrations existing in this system, in the temperature and pressure range investigated. Two methods of calculation have been employed, one depending on the combination of vapor pressure and conductivity data, and the other, on conductivity data. For both, recourse was had to the data of Campbell and Maass on the system sulphur-dioxide–water. These methods gave results that are in good agreement with each other. The existence of a complex $CaSO_3\ Ca(HSO_3)_2$ was deduced.

Hydrogen ion concentrations over the concentration and temperature range investigated have been calculated and extrapolations made to higher temperatures. These are presented in tabular form. Apart from the theoretical interest, it is pointed out that these results are of value in connection with studies of the delignification of wood by calcium-oxide–sulphur-dioxide–water solutions.

Introduction

In an earlier paper (2) a technique was described for determining vapor pressures and conductivities of the system calcium-oxide–sulphur-dioxide–water, and the data obtained were presented. Vapor pressure and conductivity values were given for a wide range of concentrations and temperatures. These values will be used in the present paper to determine hydrogen ion concentrations. Their particular interest will be discussed later on.

The system calcium-oxide–sulphur-dioxide–water can, under various conditions, contain a wide variety of compounds distributed throughout three phases. To illustrate, sulphur dioxide in the gaseous phase is in equilibrium with sulphur dioxide in the liquid phase. This is in equilibrium with sulphurous acid, which in turn is in equilibrium with its ions. On the other hand, calcium oxide combines with water to form calcium hydroxide, which is difficultly soluble in water and ionizes to some extent. Calcium hydroxide reacts with sulphur dioxide to form solid calcium sulphite. According to current ideas, calcium sulphite, virtually insoluble, forms calcium bisulphite in the presence of an excess of sulphur dioxide, calcium bisulphite existing only in solution. The complex nature of this system makes the determination of ionic concentrations difficult. In this paper only those concentrations and temperatures at which there is no solid calcium sulphite present will be considered.

The salient feature of the papers by Maass and Maass (6), Morgan and Maass (7) and Campbell and Maass (1) on the sulphur-dioxide–water equilibrium was the evidence presented to indicate that, with rise in temperature,

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[2] *Holder of a bursary and studentship under the National Research Council of Canada.*

[3] *Macdonald Professor of Physical Chemistry.*

sulphur dioxide in the liquid phase exists to a large extent as dissolved gas rather than as sulphurous acid, and that the higher the temperature the smaller is the amount of sulphurous acid present. As a result the apparent dissociation constant, K_a, of sulphurous acid decreases rapidly with increase in temperature although the true dissociation constant, K_1', may be only slightly altered. In any case the hydrogen ion concentration definitely decreases with rise in temperature. This property of the sulphur-dioxide–water system helps to give good qualitative explanation of the variation in conductivity of the system calcium-oxide–sulphur-dioxide–water with variation in calcium oxide concentration and temperature. To elucidate this the data of an earlier paper (2) are presented in Figs. 1 to 4.

In Fig. 1 it is seen that at 25° C. the hydrogen ion concentration at 0% calcium oxide is fairly large. The addition of calcium oxide increases the total number of ions, but reduces the number of hydrogen ions whose mobility is so much greater than that of the other ions that the addition of calcium oxide actually reduces the conductivity. With continued addition of calcium oxide the influence of the increase in the number of ions gradually predominates,

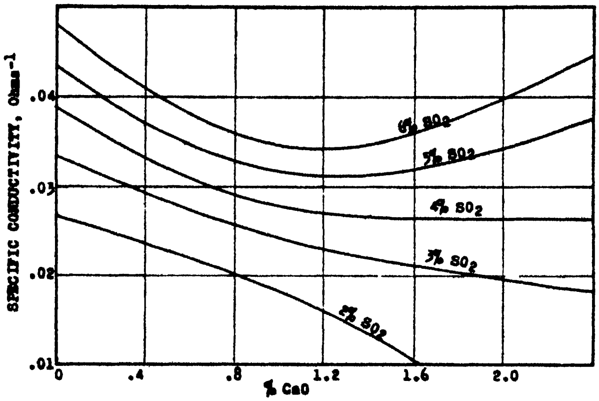


FIG. 1. *Specific conductivity—25°C.*

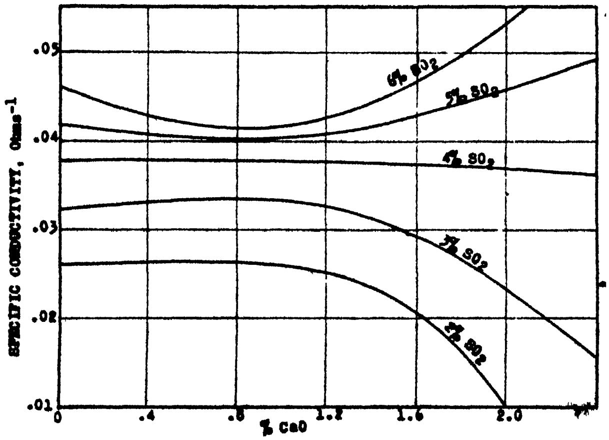


FIG. 2. *Specific conductivity—50°C.*

and therefore in the 6% and 5% sulphur dioxide curves a minimum is found. At 50° C. (Fig. 2) this minimum in the 6% and 5% curves is not so low, because at the higher temperature the initial concentration of hydrogen ions in calcium-oxide-free solution is much less. It is so much less at 70° C. (Fig. 3) and still more so at 90° C. (Fig. 4) that here the minimum disappears entirely. The reason for this is that the increase in the number of ions due to the addition of calcium oxide has the predominating influence because of the relatively fewer hydrogen ions present at the start. Furthermore, the formation of bisulphite ions due to the solution of the calcium oxide tends to decrease still further the number of hydrogen ions.

With the 4% solution, when more than 2% calcium oxide has been added the condition is reached where solid precipitates out, and, since the solid has a negative temperature coefficient, at 70° C. a maximum is reached in the conductivity values of the 4% curve. Beyond the maximum, the decrease in conductivity is due to the formation of solid which involves a reduction in the total number of ions. At the higher temperature, 90° C. (Fig. 4), this is still more pronounced. At 50° C. (Fig. 2) the 4% curve is virtually

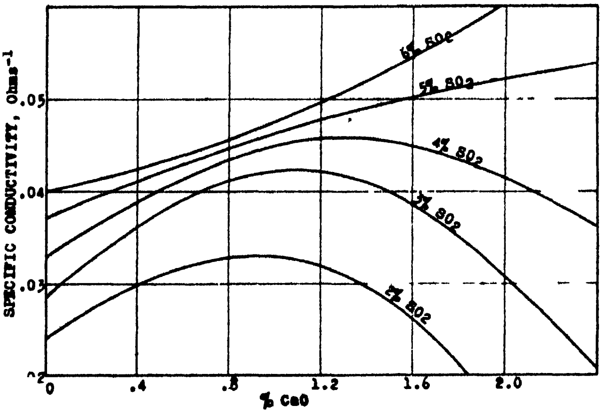


FIG. 3. *Specific conductivity—70°C.*

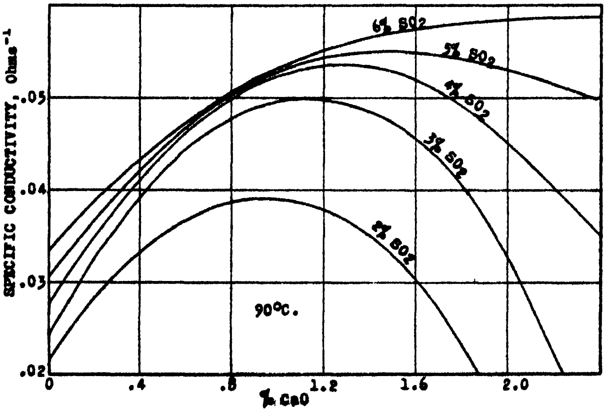


FIG. 4. *Specific conductivity—90°C.*

a straight line. To begin with, the increase in the number of ions, with the addition of calcium oxide, just compensates for the decrease in average mobility owing to the removal of hydrogen ions. Eventually in this case with continued addition of calcium oxide, precipitation of solid begins to decrease the number of ions, and at a point beyond those for which data are tabulated this curve will start to bend down, that is, show a decrease in conductivity. This is indicated in the 2% and 3% sulphur dioxide curves in this figure. It can therefore be seen that the conductivity values of the system calcium-oxide–sulphur-dioxide–water conform to the idea of decreasing hydrogen ion concentration with rise in temperature in the simpler system sulphur-dioxide–water.

It is of considerable interest to make a quantitative estimate of the magnitude of the ionic concentrations. In the first place, this will add to the knowledge of the nature of the equilibria existing in this system. In the second place, the concentration of hydrogen ions has been an important influence at higher temperatures on the physical-chemical structure of lignin. Since the system calcium-oxide–sulphur-dioxide–water is used for the delignification of wood, it is of particular interest to evaluate the hydrogen ion concentration of this system at various temperatures and under various conditions of concentration.

Hägglund and Johansson (3) have measured the rate of hydrolysis of starch, and calculated the hydrogen ion concentrations from the results of these experiments. Their results will be compared later on with those calculated by the authors.

For the calculation of the hydrogen ion concentrations from the data presented in a previous paper (2), two independent methods can be used. The first involves a combination of the vapor pressure and conductivity values. The second method depends on the information obtained from conductivities alone, provided that one takes into account the evidence, based on vapor pressure data, for the existence of a soluble calcium complex somewhat different from the commonly accepted idea of the formation of calcium bisulphite. Each method will be treated separately and then a comparison of the results will be made. The calculated hydrogen ion concentration will be discussed in connection with the role that sulphite liquor plays in the delignification of wood.

Before making any calculations a few points are worth discussing. The nomenclature used is the same as that employed by Campbell and Maass (1). Thus C_{CaO}, C_{SO_2} are the number of gram molecules of calcium oxide and sulphur dioxide respectively which are added to water to form one litre of the solution. The square brackets [ ] refer to concentrations in solution, and curved brackets ( ) are used where in the case of a divalent ion the equivalent concentration in solution is to be designated.

Part of the calculations are based on laws of equilibria which are only strictly true when the activity coefficients are unity, and as this is not the case they might be looked upon as approximations. However it may be pointed out that the results obtained are nearer the true values for the system under investigation than might at first appear. Thus Henry's law has been found by Campbell and Maass to hold with high degree of accuracy up to 12% SO_2 solution at temperatures above 25° C. (See Fig. 7 of the paper by Campbell and Maass.) Ionic concentrations are based on conductivity measurements, and equilibrium constants calculated from them were found to hold (Campbell and Maass (1)). If the fact that they hold is fortuitous owing to compensation of two factors, nevertheless the ionic concentrations will agree with those calculated from such constants.

Calculation of Hydrogen Ion Concentrations from Vapor Pressure and Conductivity Data

According to Henry's law the partial pressure of the sulphur dioxide is proportional to the concentration of the dissolved sulphur dioxide.

$$P = K_1 [SO_2]$$

The dissolved sulphur dioxide is in equilibrium with the dissolved sulphurous acid since

$$[SO_2] [H_2O] = K_2' [H_2SO_3]$$

and

$$[SO_2] = K_2 [H_2SO_3],$$

as the concentration of the water may be regarded as virtually constant for dilute solutions. The sulphurous acid is proportional to the product of the hydrogen ion and bisulphite ion concentration, since

$$H_2SO_3 = K_3' [H^+] [HSO_3^-].$$

Consequently the partial vapor pressure of the sulphur dioxide is proportional to the product

$$[H^+] [HSO_3^-].$$

When calcium oxide is dissolved by excess sulphurous acid, the calcium complex formed, if it gives rise to bisulphite ions, will increase the amount of sulphurous acid, which in turn will increase the concentration of dissolved sulphur dioxide, and this will cause an increase in the partial vapor pressure of the sulphur dioxide. Consequently the vapor pressure of an aqueous solution of sulphur dioxide should be increased when a solution containing 1 gm. mol of calcium oxide and 2 gm. mols of sulphur dioxide is added. Therefore it is possible from considerations of vapor pressure data to evaluate solutions containing equal products $[H^+]$ $[HSO_3^-]$, independently of the amount of calcium oxide that was added. Suppose a solution containing C_{CaO} gm. mols of calcium oxide has a vapor pressure P, then it follows that the product $[H^+]$ $[HSO_3^-]$ in this solution has the same value as the product $[H^+]$ $[HSO_3^-]$ of a solution containing sulphurous acid alone and having the same vapor pressure. Since the hydrogen ion concentrations of sulphurous acid solutions have been determined by Campbell and Maass (1), it is therefore possible, by having recourse to their data, to calculate the product $[H^+]$ $[HSO_3^-]$ in a sulphurous acid solution containing dissolved lime.

Apart from the accuracy with which the vapor pressures for the solutions involved have been determined, the accuracy will depend on the validity of the relation

$$[H^+][HSO_3^-] = K_1'[H_2SO_3].$$

Now although this relation will not hold over a wide range of concentrations when uncorrected concentrations are used, this aberration becomes of less importance when it is remembered that comparisons are made for solutions in which the products of the ionic concentrations are the same, and therefore the product $[H^+]$ $[HSO_3^-]$ can be evaluated with a fair degree of certainty for those solutions for which the vapor pressure data have been determined.

The conductivity, K, multiplied by 1000 is equal to the algebraic sum of the products of the ionic concentrations and mobilities, hence,

$$1000K = \mu_{Ca^{++}}(Ca^{++})^* + \mu_{HSO_3^-}[HSO_3^-] + \mu_{H^+}[H^+]$$

where $\mu_{Ca^{++}}$ = equivalent mobility of Ca ion,
(Ca^{++}) = equivalent concentration of Ca ion,
$\mu_{HSO_3^-}$ = mobility of HSO_3 ion,
$[HSO_3^-]$ = concentration of HSO_3 ion,
μ_{H^+} = mobility of H ion
$[H^+]$ = concentration of H ion.

Furthermore

$$(Ca^{++}) + [H^+] = [HSO_3^-].$$

Since a third equation is given by

$$[H^+][HSO_3^-] = S,$$

where the numerical value of S is determined from the data of Campbell and Maass (1), elimination of (Ca^{++}) and $[HSO_3^-]$ gives rise to the equation

$$(\mu_{H^+} - \mu_{HSO_3^-})[H^+]^2 - 1000\,K\,[H^+] + (\mu_{Ca^{++}} + \mu_{HSO_3^-})\,S = 0,$$

and

$$H^+ = \frac{1000K - \sqrt{(1000\,K)^2 - 4(\mu_{H^+} - \mu_{HSO_3^-})(\mu_{Ca^{++}} + \mu_{HSO_3^-})S}}{2(\mu_{H^+} - \mu_{HSO_3^-})} \qquad (1)$$

The mobilities for the hydrogen and bisulphite ions taken are those used by Campbell and Maass (1). The mobilities of the Ca ion at 25°, 50°, 70°, and 90° C. based on the International Critical Tables (4), are taken as 59.5, 90, 114 and 139 respectively.

A sample determination of (H^+) for a solution containing 1% of calcium oxide and 5% of sulphur dioxide at 50° C. is first given. The conductivity of the solution is 0.0400 (Table II, Gurd, Gishler, Maass (2)) and its vapor pressure is 75.6 cm. The concentration of a sulphurous acid solution having this vapor pressure and temperature is 3.53% (Campbell and Maass (1)). A solution having this concentration has a hydrogen ion concentration, and therefore a bisulphite ion concentration, of 0.0651, hence S has the value $(0.0651)^2$. Substituting in Equation (1), the hydrogen ion concentration is found to be 0.0236 gram mols.

* *For convenience* [ ] *will be used for mol concentrations, and* ( ) *for equivalent concentrations.*

In Table I the hydrogen ion concentrations over the range of concentrations and temperatures for which data are available, calculated by means of Equation 1, are shown.

TABLE I

HYDROGEN ION CONCENTRATIONS: VAPOR PRESSURE METHOD

% CaO	% SO_2	25°C.	50° C.	70° C.	90° C.
0	2	0.066	0.049	0.037	0.028
0	3	.081	.060	.045	.033
0	4	.095	.069	.051	.037
0	5	.109	.077	.056	.041
0	6	.122	.084	.061	.045
0.5	2	.0140	.0106	.0065	.0033
0.5	3	.0282	.0158	.0100	.0053
0.5	4	.0417	.0227	.0134	.0074
0.5	5		.0312	.0178	.0099
0.5	6		.0457	.0235	.0130
1.0	2	0079	.0045	.0033	.00097
1.0	3	.0192	.0097	.0049	.0028
1.0	4	.0362	.0157	.0085	.0045
1.0	5		.0236	0125	.0068
1.0	6		.0352	0173	.0093
1.5	3	.0142	.0044	.0020	.00079
1.5	4	.0250	.0094	.0054	.0033
1.5	5	.0382	.0147	.0086	.0054
1.5	6		.0204	.0119	.0074
2.0	4	.0121	.0041	.0035	.0027
2.0	5	.0172	.0078	.0059	.0049
2.0	6	.0238	.0105	.0078	.0054

Calculation of Hydrogen Ion Concentrations from Conductivity Data

Instead of using the vapor pressures of solutions of calcium-oxide–sulphur-dioxide–water to evaluate the product $[H^+]$ $[HSO_3^-]$ from Campbell and Maass's data, the relation

$$K_a = \frac{[H^+]\,[HSO_3^-]}{[SO_2] + [H_2SO_3]}$$

can be used, since the equilibrium upon which this equation is based also exists in the presence of the dissolved calcium oxide. The numerical values for K_a have been determined by Campbell and Maass (1), and it is evident from their data that within experimental error, K_a is constant at a given temperature over a wide range of concentrations. If C_{SO_2} is the number of gram mols of sulphur dioxide in the solution in which all the calcium oxide has been dissolved then

$$C_{SO_2} = [SO_2] + [H_2SO_3] + 2[Ca(HSO_3)_2] + [HSO_3^-]\,.$$

If the solution of the lime or calcium sulphite is due to the formation of calcium bisulphite then

$$Ca(HSO_3)_2 \rightleftharpoons Ca^{++} + 2HSO_3^-\,.$$

The concentration of the HSO_3^- may be written

$$C_{HSO_3^-} = \alpha[HSO_3^-] + \beta[HSO_3^-],$$

where α is the fraction of the bisulphite ion associated with hydrogen ions and β the fraction associated with calcium ions, so that

$$\beta[HSO_3^-] = 2[Ca^{++}]$$

and

$$\alpha[HSO_3^-] = [H^+]$$

Furthermore

$$C_{CaO} = [Ca(HSO_3)_2] + [Ca^{++}]$$

Hence

$$\begin{aligned} [SO_2] + [H_2SO_3] &= C_{SO_2} - 2\,[Ca(HSO_3)_2] - \beta[HSO_3^-] - \alpha[HSO_3^-] \\ &= C_{SO_2} - 2\,C_{CaO} - \alpha[HSO_3^-] \\ &= C_{SO_2} - 2\,C_{CaO} - [H^+]\,. \end{aligned}$$

The equation

$$K_a = \frac{[H^+]\,[HSO_3^-]}{[SO_2] + [H_2SO_3]}$$

becomes, in the presence of lime,

$$K_a = \frac{[H^+]\,\{\alpha[HSO_3^-] + \beta[HSO_3^-]\}}{C_{SO_2} - 2\,C_{CaO} - [H^+]}$$

and this becomes

$$K_a = \frac{H^+\,([H^+] + 2\,[Ca^{++}])}{C_{SO_2} - 2C_{CaO} - [H^+]}\,.$$

Rearranging this we get

$$[H^+]^2 + (2\,[Ca^{++}] + K_a)\,[H^+] - (C_{SO_2} - 2C_{CaO})K_a = 0\,.$$

As before

$$1000K = \mu_{Ca^{++}}(Ca^{++}) + \mu_{H^+}[H^+] + \mu_{HSO_3^-}\,\alpha[HSO_3^-] + \mu_{HSO_3^-}\,\beta[HSO_3^-]$$

where

$$2\,[Ca^{++}] = (Ca^{++})$$

$$1000K = (\mu_{Ca^{++}} + \mu_{HSO_3^-})\,(Ca^{++}) + (\mu_{H^+} + \mu_{HSO_3^-})\,[H^+]$$

By combining the above two equations

$$[H^+]^2 + \left[\frac{1000\,K}{\mu_{Ca^{++}} + \mu_{HSO_3^-}} - \frac{\mu_{H^+} + \mu_{HSO_3^-}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\,[H^+] + K_a\right][H^+] - (C_{SO_2} - 2C_{CaO})K_a = 0\,.$$

$$[H^+]^2 + \frac{1000K[H^+]}{\mu_{Ca^{++}} + \mu_{HSO_3^-}} - \frac{\mu_{H^+} + \mu_{HSO_3^-}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\,[H]^2 + K_a[H^+] - (C_{SO_2} - 2\,C_{CaO})K_a = 0$$

$$\left(\frac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)[H^+]^2 + \left(\frac{1000K + (\mu_{Ca^{++}} + \mu_{HSO_3^-})\,K_a}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)[H^+] - (C_{SO_2} - 2\,C_{CaO})K_a = 0$$

$$[H^+] = \frac{-\left(\dfrac{1000K + (\mu_{Ca^{++}} + \mu_{HSO_3^-})K_a}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)}{2\left(\dfrac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)} + \frac{\sqrt{\left(\dfrac{1000K + (\mu_{Ca^{++}} + \mu_{HSO_3^-})K_a}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)^2 + 4\left(\dfrac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)\left(C_{SO_2} - 2C_{CaO}\right)K_a}}{2\left(\dfrac{\mu_{Ca^{++}} - \mu_{H^+}}{\mu_{Ca^{++}} + \mu_{HSO_3^-}}\right)} \qquad (2)$$

When Equation (2) is used to calculate ionic concentrations, the values found are less than those obtained with Equation (1). To illustrate this a few comparisons are made in Table II.

TABLE II

COMPARISION OF $[H^+]$ CALCULATED BY MEANS OF EQUATIONS 1 AND 2 FOR SOLUTIONS OF 1% CALCIUM OXIDE AND 4% SULPHUR DIOXIDE

Temp., ° C.	25	50	70	90
Equation 1	0.0362	0.0157	0.0085	0.0045
Equation 2	.0207	.0115	.0064	.0036

The differences are not very large and it would be an achievement to make it possible to evaluate the hydrogen ion concentration to this degree of accuracy above 50° C. Nevertheless, a reason for this difference can be found. Equation (2) is based on the assumption that calcium sulphite dissolves to form calcium bisulphite. If this is the case then a homogeneous liquid phase cannot be formed until the sulphur dioxide concentration is at least such that

$$2\,C_{SO_2} = C_{CaO}$$

It was observed that complete solution sometimes took place before this sulphur dioxide concentration was reached. Again if calcium bisulphite, only, is formed, the vapor pressure of solutions containing less sulphur dioxide than that given by

$$2\,C_{SO_2} = C_{CaO}$$

should be, if anything, less than that of water, whereas in the sulphur dioxide concentration range between $C_{SO_2} = C_{CaO}$ and $2C_{SO_2} = C_{CaO}$ the vapor pressures are markedly greater than those of water. This is illustrated in Fig. 5 in which the partial vapor pressures of sulphur dioxide are represented in terms of the ratio C_{SO_2}/C_{CaO}.

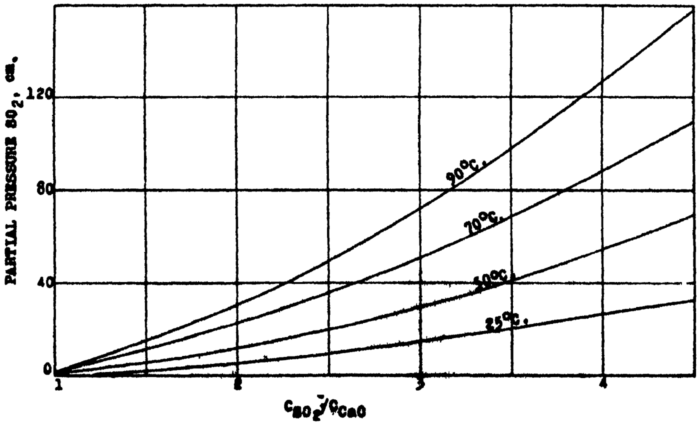
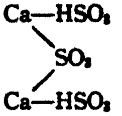


FIG. 5. *Partial pressure SO_2—1% CaO.*

From a consideration of the vapor pressures it seems obvious that a soluble complex containing a smaller amount of sulphur dioxide than is given by the ratio C_{CaO} to $2C_{SO_2}$ is formed. Since stoichiometric proportions must be retained, it is pertinent to examine the evidence of a complex depending on the ratio $1C_{CaO}$ to $1.5C_{SO_2}$. To such a complex the structural relation



might be assigned. While not advocating one way or another the fundamental basis of Langmuir's concept of the structure of the atom (5), the authors do believe that the postulates advanced by Langmuir indicate the possibility of the existence of a molecular structure, and according to Langmuir's postulates the above structure is a possible one.

A comparison of vapor pressures of solutions containing calcium oxide and sulphur dioxide in aqueous solution with those containing only sulphur dioxide in aqueous solution, can be used to determine whether the formation of the above complex is probable. For instance, using the above structure, a solution containing 0.5% of calcium oxide and 3% of sulphur dioxide at 25° C. should contain 2.14% of free sulphur dioxide. This is the vapor pressure of a 2.1% sulphur dioxide solution, as found by Campbell and Maass (1). A large number of similar cases were examined and found to conform with the above structure. A number of these are included in Table III.

TABLE III

Temp., °C.	V. p., cm.	SO_2 %
CaO—0.5%	Total SO_2—3%	Free SO_2—2.14%
25	19	2.1
50	46.5	2.1
70	88	2.08
90	140	1.93
CaO—1.0%	Total SO_2—4%	Free SO_2—2.3%
25	24	2.2
50	52	2.33
70	91	2.20
90	152	2.2
CaO—1.5%	Total SO_2—5%	Free SO_2—2.43%
25	29	2.3
50	56.5	2.6
70	105	2.6
90	180	2.8
CaO—2.0%	Total SO_2—6%	Free SO_2—2.58%
50	55	2.6
70	110	2.8
90	210	3.4

The results given cover the temperature range 25° to 90°.C. and the concentration range passes diagonally across the entire range of concentrations studied. Above each section of Table III the concentration of calcium oxide and sulphur dioxide is given, together with the amount of uncombined sulphur dioxide based on a ratio $1C_{CaO}$ to $1.5C_{SO_2}$. The three columns of each section contain the temperature, the vapor pressure for the given concentration and temperature, and finally, the concentration of sulphur dioxide required according to Campbell and Maass's (1) data to produce the vapor pressure shown in Column 2. On the basis of a 2 to 1 ratio, the amount of free sulphur dioxide would be very different, 1.86 as compared to 2.14% for a solution containing 0.5% calcium oxide and 3% sulphur dioxide; 1.83 as compared to 2.3% for a 1% calcium oxide and 4% sulphur dioxide, and so on.

There is one marked exception to the general agreement. This is found at the end of the last section (CaO 2%, SO_2 6%, at 90° C.). The free sulphur dioxide found was 3.4%, which is considerably higher than the estimated value. At the precipitation temperature there is a marked increase in the slope of the vapor pressure curve. Therefore at a concentration and temperature within the precipitation range, this relation cannot hold. This is also found, but to a lessened degree, in the section immediately above that under discussion. A discussion of the phenomenon of precipitation must be left for a later paper.

On the above evidence therefore it can be assumed that there is evidence for the formation of

$$CaSO_3 . Ca(HSO_3)_2 ,$$

and the influence of this concept on the evaluation of the hydrogen ion concentration by Equation (2) will now be shown. Without considering the matter in as great detail as that given above, the following equations may be listed.

$$C_{SO_2} = [SO_2] + [H_2SO_3] + 3[Ca_2SO_3(HSO_3)_2] + [Ca_2SO_3^{++}] + \alpha[HSO_3^-] + \beta[HSO_3^-]$$

$$C_{CaO} = 2[Ca_2SO_3(HSO_3)_2] + 2[Ca_2SO_3^{++}]$$

$$2[SO_2] + 2[H_2SO_3] = 2C_{SO_2} - 6[Ca_2SO_3(HSO_3)_2] - 2[Ca_2SO_3^{++}] - 2\alpha[HSO_3^-] - 2\beta[HSO_3^-]$$

$$[SO_2] + [H_2SO_3] = C_{SO_2} - 1.5C_{CaO} + 2[Ca_2SO_3^{++}] - \alpha[HSO_3^-] - \beta[HSO_3^-].$$

As before

$$2[Ca_2SO_3^{++}] = \beta[HSO_3^-]$$

and

$$[H^+] = \alpha[HSO_3^-].$$

Hence Equation (2) becomes

$$[H^+] = \frac{-\left(\dfrac{1000K + (\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})K_a}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}\right)}{\dfrac{2(\mu_{Ca_2SO_3^{++}} - \mu_{H^+})}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}} + \frac{\sqrt{\left(\dfrac{1000K + (\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})K_a}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}\right)^2 + \dfrac{4(\mu_{Ca_2SO_3^{++}} - \mu_{H^+})}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}\,(C_{SO_2} - 1.5C_{CaO})\,K_a}}{\dfrac{2(\mu_{Ca_2SO_3^{++}} - \mu_{H^+})}{(\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})}} \quad (3)$$

Equation (3) is identical with Equation (2), except that $C_{SO_2} - 2C_{CaO}$ is replaced by $C_{SO_2} - 1.5C_{CaO}$, and that $\mu_{Ca^{++}}$ is replaced by $\mu_{Ca_2SO_3^{++}}$. The mobility of the $Ca_2SO_3^{++}$ ion is unknown, but there is probably little error in assigning to this ion a mobility the same as that of the calcium ion. It is as if the calcium ion carries along with it a calcium sulphite molecule, and the assumption is that the hydration of both ions is such that the additional weight is of no material importance. In any case the mobility of the hydrogen ion is so much greater than that of the other ions that the use of the mobility of the calcium ion for the supposed $Ca_2SO_3^{++}$ ion will not introduce any large error.

It may be worth noting that the imposing appearance of Equation (3) does not mean that intricate and new ideas have been employed in its deduction. The apparently involved calculations can be considerably simplified since certain terms such as

$$(C_{SO_2} - 1.5C_{CaO}); \quad (\mu_{Ca_2SO_3^{++}} + \mu_{HSO_3^-})$$

etc., have constant values for certain temperatures and concentrations. However, for the presentation of the relation the replacement of such terms by constants which would then have to be defined, would not add to the simplification of its representation.

Before tabulating the values obtained for the hydrogen ion concentration as calculated by Equation (3), it should be mentioned that if the complex $CaSO_3.Ca(HSO_3)_2$ is only partially dissociated, so far as bisulphite ions are concerned, an equation identical with Equation (3) would be obtained except that the mobility of the ion $CaSO_3.Ca(HSO_3)^+$ would have to replace that of the $Ca_2SO_3^{++}$ ion.

TABLE IV

Hydrogen ion concentration—C_{SO_2}—1.5 C_{CaO}

% CaO	%SO₂	25° C.	50° C.	70° C.	90° C.
0.5	2	0.0165	0.0106	0.0063	0.0039
0.5	3	.0328	.0158	.0099	.0055
0.5	4	.0511	.0238	.0141	.0091
0.5	5		.0335	.0180	.0123
0.5	6		.0465	.0229	.0155
1.0	2	.0048	.0024	.0014	.0010
1.0	3	.0191	.0099	.0051	.0031
1.0	4	.0354	.0160	.0109	.0055
1.0	5		.0233	.0123	.0077
1.0	6		.0328	.0163	.0106
1.5	3	.0060	.0033	.0018	.0010
1.5	4	.0185	.0092	.0053	.0032
1.5	5	.0282	.0148	.0085	.0055
1.5	6	.0403	.0202	.0113	.0074
2.0	4	.0064	.0038	.0022	.0014
2.0	5	.0149	.0082	.0055	.0035
2.0	6	.0232	.0097	.0074	.0055

Discussion

A comparison of the hydrogen ion concentrations as evaluated by Equations (1) and (3) shows excellent agreement at those concentrations and temperatures at which experimental data are such that this agreement might be expected, if both equations are based on a sound foundation. This is the case with the values obtained at 50, 70 and 90° C. where concentrations are such that the solid phase is absent. This is not the case with a few 90° C. values having a relatively high CaO/SO_2 ratio. At that temperature and calcium oxide concentration, partial precipitation takes place, and, of course, with the appearance of the solid phase, Equations (1) and (3) do not hold. The question of precipitation temperatures will be dealt with in a later paper.

Apart from this, the greatest discrepancy is to be found with some of the values at 25° C. at 1.5 and 2.0% of calcium oxide concentration. With these the partial vapor pressures of sulphur dioxide are so small that the experimental error in vapor pressure determination is sufficient to account for the discrepancy. On the other hand, the conductivity values in this region are more accurate. The reverse is true at high temperatures. Consequently in weighing the relative merits of the values for hydrogen ion concentration given in Tables I and IV, greater weight should be given to those in Table I for temperatures of 70 and 90° C., whereas for temperatures of 25 and 50° C. greater weight should be given to Table IV.

It was pointed out in a previous paper (2) that the greatest extrapolation of data was made with the 0.5% calcium oxide concentration, and consequently the values for hydrogen ion concentrations deduced at that concentration will not be quite as accurate as those for the higher calcium oxide concentrations. From an experimental point of view, the data in the neighborhood of 1% CaO may be taken as the most accurate. From the data available, bisulphite ion concentration can also be calculated. This has been omitted however in order not to unduly lengthen the paper.

One of the main points of interest concerning the hydrogen ion concentrations is, as was shown in an investigation the results of which are to be published shortly, that there is an optimum hydrogen ion concentration at

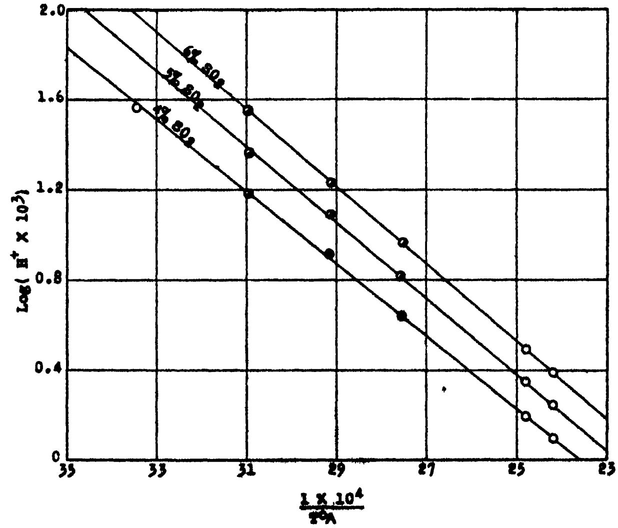


FIG. 6. *Hydrogen ion concentrations—1·0% CaO.*

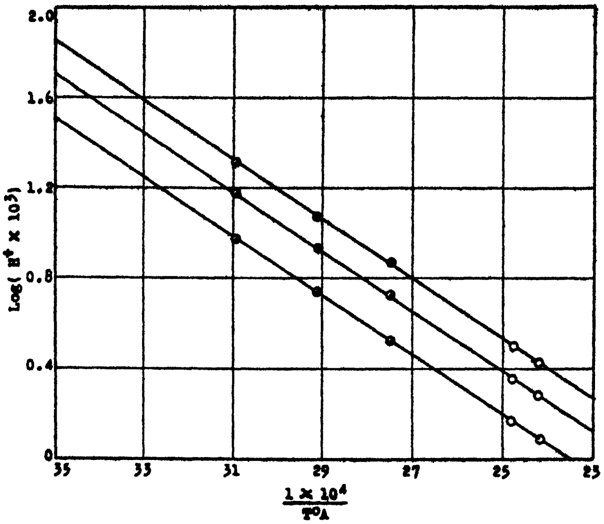


FIG. 7. *Hydrogen ion concentrations—1·5% CaO.*

which the lignin in wood when heated above 130° C. is not changed into a condition in which the delignification cannot be brought about readily by the system calcium-oxide–sulphur-dioxide–water.

The data for hydrogen ion concentrations have been established only up to 90° C. but it is possible to extrapolate by plotting log $[H^+]$ against $1/T$. This has been done for solutions containing 4, 5 and 6% SO_2, and 1 and 1.5% CaO (Figs. 6 and 7). Between 25 and 90° C. the above relation is linear and therefore it is reasonable to expect that extrapolated values will be fairly accurate. In Table V the hydrogen ion concentrations are given at 130 and 140° C.

TABLE V

HYDROGEN ION CONCENTRATIONS—EXTRAPOLATED VALUES

	Temp., °C.	0% CaO	1% CaO	1.5% CaO
4% SO_2	130	0.020	0.0016	0.0012
	140	.017	.0013	.0010
5% SO_2	130	.022	.0025	.0022
	140	.019	.0020	.0018
6% SO_2	130	.024	.0032	.0032
	140	.021	.0025	.0027

In a paper by Hägglund and Johansson (3) to which reference has already been made, the rate of hydrolysis of starch solutions containing 5% of sulphur dioxide and 1.24 and 0.8% calcium oxide has been measured. This was carried out during the cooking of wood, over a temperature range of 60 to 130° C. It is not quite clear from their paper as to the temperature at which the hydrogen ion concentration was measured at the start of the cook, but as they mentioned that the hydrolysis of the starch was measured between 110 and 120° C. it is assumed that the hydrogen ion concentrations obtained refer to those at that temperature. If that is the case, the values that they obtained—0.00437 for the 1.24% calcium oxide solution and 0.00479 for the 0.8% calcium oxide— compare fairly well with those calculated from the data of the authors for these concentrations at 115° C., namely 0.0033 and 0.0039 respectively.

Hägglund indicates that the evidence of Campbell and Maass for the low hydrogen ion concentration of sulphurous acid at high temperatures, and consequently the still lower hydrogen ion concentrations in the presence of calcium oxide, were not truly representative of the hydrogen ion concentration during the cooking of wood, owing to the formation of sulphonic acids. Campbell and Maass recognized this. In the presence of wood, complications such as the relatively greater absorption of free sulphur dioxide compared with that of fixed sulphur dioxide occur, as was shown by Saunderson and Maass (8).

So far as the application of the hydrogen ion concentration data established in this paper to the practical process of the delignification of wood is concerned, the obtaining of the data in this paper must be looked upon as a first step in this direction. It may be pointed out that the action of the calcium oxide is such as to produce something analogous to that of a buffer solution. The influence of sulphonic acids on the equilibria that have been discussed above is the subject of a further investigation. As the present paper has for its main object the presentation of the physical chemical equilibria that exist in the system calcium-oxide–sulphur-dioxide–water, a detailed discussion of the application of the results to the delignification of wood by sulphite liquor will be left for later papers dealing with this phase of the subject.

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HYDROGENATIONS IN A TETRALIN MEDIUM

I. DESTRUCTIVE HYDROGENATION OF BITUMEN AND PITCH[1]

By E. H. Boomer[2] and J. Edwards[3]

Abstract

The importance of a suspension medium in processes of destructive hydrogenation is discussed, with particular reference to the efficiency of the medium as a hydrogen carrier. The value of tetralin as a medium, in that it is a good solvent, is stable to heat, and acts as a hydrogen carrier, has been determined in the hydrogenation of bitumen and stable pitch. Tetralin does not cause an increase in yield of oil but does improve the quality somewhat. It increases the rate of hydrogenation of bitumen but does not affect that of stable pitch.

Introduction

Previous reports from this laboratory (2, 3) on the destructive hydrogenation of coal have shown the importance of the suspension medium in such processes. Within the limits of the work, it was found that the medium was fully as important as any added solid catalyst. Consideration of the reactions involved suggests that such a result might be expected. As the term implies, destructive hydrogenation involves two principal reactions; namely, thermal decomposition and hydrogenation. Both reactions are concurrent and take place until substances resistant to further action are produced, but the reactions differ fundamentally in their basic characteristics (9). Thermal decomposition is irreversible and proceeds to completion, yielding gas and coke, the velocity of the reaction increasing rapidly with rising temperature. The reaction may be described as a monomolecular decomposition accompanied by polymerization of the products. In contrast, the hydrogenation reaction is reversible and is relatively less sensitive to temperature changes. Generally, equilibrium is shifted towards dehydrogenation with rising temperature and decreasing hydrogen concentration.

Satisfactory control of destructive hydrogenation requires that thermal decomposition should produce unsaturated molecular fragments at such a rate that these fragments may be stabilized by hydrogenation before polymerization can take place. The implied mechanism, that stabilization of the products of decomposition occurs through hydrogenation, has been found

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satisfactory and coincides with the views of Tropsch (14), Kling and Florentin (10) and Kiss (9). Waterman and Perquin (15), supported by Bruylants' (4) work on coke-oven tars, suggest from a consideration of their results with paraffin wax the view that the primary products of decomposition are stable, and the function of the hydrogen is the prevention of dehydrogenation to unstable bodies capable of polymerization. The appreciable absorption of hydrogen, either gaseous or from the medium, observed in this work makes it probable that Waterman's mechanism plays a minor part in the process.

Assuming the first mechanism, ideal conditions of operation would require a low temperature, a high concentration of reacting substances and catalysts capable of promoting both reactions. At the temperatures used, the rate of hydrogenation of unsaturated molecular fragments must be very great; thus a catalyst capable of promoting hydrogenation is unnecessary. On the other hand, the provision of a high concentration of reactants and the use of a catalyst to ensure adequate supplies of decomposition products at comparatively low temperatures are essential. In this regard, Tropsch (14) and Kling and Florentin (10) have suggested that the primary function of the catalyst is the promotion of the thermal decomposition reaction. The suspension medium offers an excellent means of fulfilment of these conditions by acting as a solvent for the raw material, the thermal decomposition products and hydrogen. A large number of substances may be suggested, but an ideal substance would also act as a hydrogen carrier by maintaining a supply of combined hydrogen greatly in excess of that possible in true solution. Such ideal substances should be capable themselves of rapid reversible hydrogenations. Tetralin (1,2,3,4-tetrahydronaphthalene) is typical of such substances and fulfils the requirements to a large degree.

Tetralin is readily prepared from naphthalene by hydrogenation (13) even on a commercial scale. Hall (6) and others (7, 11) have examined the reaction between hydrogen, naphthalene and tetralin at temperatures as high as 500° C., or higher, and have found that a catalyst is essential. Tetralin is the principal constituent of the equilibrium mixture at 400° C., while decalin appears in small quantities at higher temperatures. Both tetralin and decalin are fairly stable at 400° C., while naphthalene is stable at higher temperatures. Cracking of tetralin to benzene and related compounds is slight at 400° C. and extensive at 450° C. and independent of the presence of a catalyst, excepting the cracking type such as aluminium chloride. It may, therefore, be concluded that tetralin, naphthalene and hydrogen will participate in a rapid reversible reaction at temperatures of about 400° C. in the presence of hydrogen at high pressures and a catalyst like molybdic oxide. The hydrogen atoms in the 1, 2, 3, 4 positions in tetralin are in a highly active state and represent a concentration of two gram molecules of available hydrogen per gram molecule of medium.

The superior action of tetralin as a suspension medium and its ability to hydrogenate coal in the absence of free hydrogen have been reported (2, 3), and are clearly consequences of its unique properties as described. Undoubtedly other compounds of a similar nature and value in destructive hydrogenation exist, as a study of patent literature attests, but it is doubtful whether any fulfil the requirement to a degree comparably with tetralin.

In order to confirm the value of tetralin as a suspension medium and to extend the field of application, investigations have been carried out on a number of materials. In what follows, the use of tetralin in the hydrogenation of McMurray bitumen and pitches resulting from distillation of hydrogenated bitumen and coal will be described. The hydrogenation of bitumen in the presence of a variety of catalysts has been reported (1). The material absorbs hydrogen rapidly with the production of light oils. Distillation of the oil and repeated hydrogenation of the residual oils yielded an asphaltic residue, about 15% of the bitumen, that was highly resistant to destructive hydrogenation. In general the heavy oils and pitches resulting from the distillation of hydrogenated bitumen showed great thermal stability and resistance to hydrogenation. The thermal stability, at atmospheric pressure, of the pitches obtained from hydrogenated coal has been remarked upon (2).

Experimental data on the hydrogenation of stable coal tars have been presented by King and Mathews (8) and by Morgan and Veryard (12). According to Morgan the hydrogenation of otherwise resistant residues may be brought about by the use of molybdic oxide and sulphur as catalytic agents in a very high concentration of hydrogen. The effectiveness of this catalyst was shown by King in the continuous hydrogenation of coal tars and of their residues from previous hydrogenation. The most effective means of obtaining rapid and complete reduction to oils was found to be vapor phase hydrogenation at temperatures as high as 500° C.

Materials, Apparatus and Procedure

Bitumen, supplied through the kindness of Dr. K. A. Clark of the Research Council of Alberta, was prepared from McMurray bituminous sands (5). The bitumen was dehydrated by heating it at 110° C. until evaporation of water ceased; it contained 1.5% mineral matter. Its composition has been given (1).

Oils obtained by hydrogenating bitumen were distilled according to the A.S.T.M. gasoline test; the end point of the distillation was 300° C. The pitch-like residues obtained in a number of experiments were combined and this composite pitch was used in the work to be described. The pitch was soft at room temperature and could be distilled to 400° C. at atmospheric pressure without decomposition.

Two types of pitches were obtained from hydrogenated coal exactly as described above (by distillation to 300° C.). One type of pitch was made up of all the residues obtained in experiments in which tetralin was used as suspension medium for coal. This pitch was solid at room temperature and extraordinarily stable to heat. The other type of pitch was made up of residues from experiments in which liquid petrolatum was used as medium (3). This pitch was soft at room temperature and slightly less stable to heat.

The tetralin was Eastman's Practical Grade, b.p. 202–204° C.

The catalyst used throughout was molybdic oxide, prepared by roasting ammonium molybdate and grinding it to pass a 100 mesh screen.

Commercial electrolytic hydrogen as supplied in steel cylinders was used. The apparatus, including the 1800 cc. rocking autoclave with accessories, has been described (1) in detail.

The procedure was identical with that employed in the hydrogenation of coal (3). Weighed amounts of material and medium were thoroughly mixed with the required amount of catalyst and introduced into the autoclave. Hydrogen was admitted until the pressure was that at which it was desired to operate, and the temperature of the autoclave was raised to the operating temperature, which was maintained constant for four hours. The autoclave was then cooled, the gases were withdrawn and fresh hydrogen was admitted. The autoclave was heated for a second period of four hours, and cooled. The gases were then withdrawn, and the autoclave was opened. The liquid and solid products were weighed, separated, and the liquids distilled. The gases were stripped in charcoal absorbers and analyzed.

Results and Discussion

The results of experiments with bitumen and pitch are shown in Tables I and II. The values for hydrogen absorbed, gas produced and the yields of oil, coke and gas are given by weight and based on bitumen or pitch, as the case may be, correction being made for added catalyst and tetralin. The distillation data constitute an exception in being based on the total oil recovered. In these calculations it was assumed that tetralin did not absorb hydrogen or suffer any decomposition or loss. All losses have been assigned arbitrarily to that part of the initial charge consisting of bitumen or pitch. This procedure gives somewhat less favorable results than may be true regarding the production of oil.

Bitumen

The results obtained in Experiments 178 and 179 show that there is little advantage in the use of tetralin. Hydrogen absorption is higher, but coke and gas formation are also higher and the oil yield is lower with tetralin. The lower oil yield may be accounted for in the high loss recorded in Experiment 179.

The oil obtained in Experiment 179 appears to be of a better quality, but the difference in properties may be explained by the presence of tetralin. The yields of pitch, when calculated to a bitumen basis, are almost identical in the two experiments. Evidence of more complete reaction in the presence of tetralin is given by the formation of hydrogen sulphide. Without tetralin, about 33.5% of the sulphur content of the bitumen was removed as hydrogen sulphide. With tetralin, 51% of the sulphur appeared as hydrogen sulphide.

Examination of the pressure-temperature-time records of the experiment shows definitely that better results are obtained when tetralin is used. Fig. 1 gives the pressure-time record for Experiments 178 and 179. The rate of reaction with tetralin is very much greater, about twice that with bitumen alone, although the pressure drop is much the same in both cases. The action of tetralin may be likened to that of a catalyst in increasing the velocity, without altering substantially the extent, of reaction.

In Experiment 180, tetralin was used as a hydrogenating agent in the absence of hydrogen. Natural gas, 93% methane with traces of ethane and propane and 5% nitrogen, was used in place of hydrogen to create the required high pressure. A considerable quantity of gas, including a small amount of hydrogen, was produced in the reaction and a considerable amount

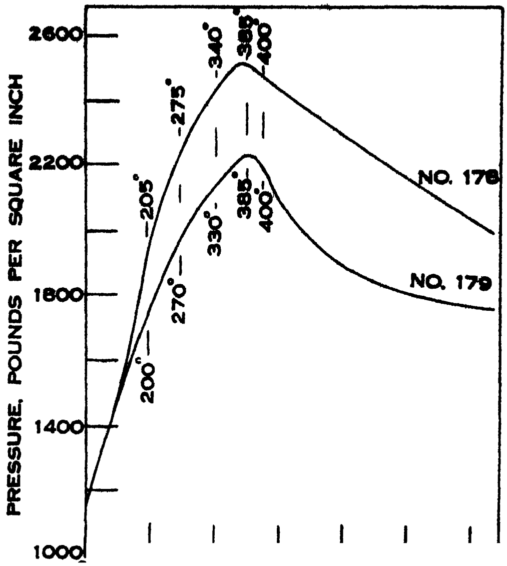

FIG. 1. *Pressure-time relations showing temperatures for the first cycles in the hydrogenation of bitumen with and without tetralin.*

TABLE I

HYDROGENATION OF MCMURRAY BITUMEN IN THE PRESENCE OF TETRALIN AT 400° C.

Gas	Hydrogen		Natural gas
Experiment No.	178	179	180
Bitumen, gm.	391	294	302
Tetralin, gm.	0	110	104
Average pressure, lb. per sq. in.			
Initial, cold	1115	1060	1035
Maximum, hot	2575	2450	3510
Final, cold	770	795	1105
Pressure change	−345	−265	70
Hydrogen absorbed, % of bitumen	2.0	2.3	—
Gas produced, l. per kg. bitumen	57.7	82.1	185
Gas—Hydrogen, %	81.6	80.2	3.4
—Hydrogen sulphide, %	3.1	3.6	1.0
Yields, basis bitumen			
Oil, %	85.0	78.0	36.8
Solid, %	6.0	6.7	22.2
Charcoal absorber, %	2.1	2.7	6.3
Gas, %	4.2	4.8	20.4
Loss, %	2.7	7.8	14.3
Oil analysis			
Density	.9236	.9341	.9603
Viscosity, 25° C., poises	.445	.134	.027
Soluble in H_2SO_4, %	50	64	54
Carbon residue, %	6.18	2.83	4.9
Distillation of total oil			
Over at 175° C., %	10.5	9.1	6.3
Over at 225° C., %	16.5	41.3	43.7
Over at 300° C., %	33.0	52.0	57.8
Pitch, %	67.0	48.0	42.2

NOTE:—*Two treatments of four hours each. Catalyst, 5% MoO_3 (by weight).*

of cracking was evident from the high coke yield and fluid nature of the oil. Most of the hydrogen was produced during the first treatment. On distillation the oil showed a naphthalene content of 33.6%, recovered as crystals. This amounts roughly to 50% of the tetralin used. Gaseous hydrogen recovered amounted to 0.675 gm., which corresponds to 22.3 gm. of tetralin. Evidently more than half of the hydrogen content of the reduced tetralin reacted with the oils. Assigning all this hydrogen to the bitumen, the absorption was 0.3%. Undoubtedly the tetralin yielded hydrogen to the bitumen and probably to a greater extent than 0.3%.

In conclusion, it may be said that tetralin acts as a catalyst in the destructive hydrogenation of bitumen. Its presence is beneficial from the point of view of increasing the rate of reaction rather than of increasing the conversion to oils.

Pitches

The results of experiments on the hydrogenation of pitches recovered from hydrogenated bitumen and coal are given in Table II.

It was shown previously (1) that the pitch obtained from hydrogenated bitumen possessed great stability, and could be decomposed and hydrogenated only in the presence of aluminium chloride at 460 to 500° C. Experiments 176 and 177 were comparative experiments on such a pitch, with and without the addition of tetralin. There was a noticeable gain in oil yield and decrease in coke and gas yield in the presence of tetralin. The pressure-time and pressure-temperature charts failed to show any difference in the rate of reaction. The benefits apparent in Experiment 177 are not all real, however, since the yield of pitch, based on bitumen, is greater. It may be concluded that the use of tetralin is of no great benefit.

The hydrogenation of pitches recovered from hydrogenated coal was also carried out with and without tetralin. The results (Experiments 172 to 175) are shown in Table II. The temperature, 450° C., employed in these experiments was the only condition that differed from the conditions existing in the experiments discussed above. This difference is significant, however, since Hall (6) has shown that the decomposition of tetralin under such conditions is appreciable.

Contrary to expectations, tetralin had no great effect on the hydrogenation of the less stable pitch obtained from coal and petrolatum. A higher hydrogen absorption and production of a better quality oil in the presence of tetralin suggested that the reaction was not the same in each case, but no difference in rate of reaction was discernible in the pressure-time-temperature records.

With regard to Experiments 173 and 174, in which pitch obtained from hydrogenated coal and tetralin mixtures was treated, the results offer some evidence of a beneficial action due to tetralin. The yield of oil, based on bitumen alone after subtracting the added tetralin, was more than 71% in Experiment 173, compared with 67% in Experiment 174. Hydrogen absorption was greater and coke formation less on the same basis in the presence of

TABLE II

HYDROGENATION OF PITCHES IN THE PRESENCE OF TETRALIN

Pitch type	From bitumen		From coal and petrolatum		From coal and tetralin	
Experiment No.	176	177	172	175	174	173
Pitch, gm.	399	293	390	356	387	268
Tetralin, gm.	0.0	98	0.0	42	0.0	129
Temperature, °C.	420	420	450	450	450	450
Average pressures, lb. per sq. in.						
Initial, cold	1100	1060	930	1135	1065	1035
Maximum, hot	2360	2500	2245	2740	2495	2360
Final, cold	640	750	670	820	555	610
Pressure change	−460	−310	−260	−315	−510	−425
H_2 absorbed, % of pitch	2.4	2.3	1.6	2.3	2.8	3.4
Gas produced, l. per kg. pitch	75.6	61.3	48.6	95.0	90.6	156.0
H_2 in gas, %	71.7	82.3	83.0	72.8	62.2	71.8
Yields, basis pitch						
Oil, %	84.3	94.2	89.5	87.0	67.2	71.7
Solid, %	5.8	3.5	0.0	0.9	13.9	5.3
Charcoal absorber, %	2.7	2.4	1.3	3.9	2.1	4.5
Gas, %	6.8	3.9	3.3	9.6	9.3	11.3
Loss, %	0.4	Gain	5.9	Gain	7.5	7.2
Distillation of total oil						
Over at 175° C., %	3.1	2.3	4.7	13.5	1.6	6.6
Over at 225° C., %	6.6	22.4	8.0	28.2	8.6	30.7
Over at 300° C., %	17.2	36.7	21.1	50.0	22.5	43.1
Pitch, %	80.5	63.2	78.9	49.6	76.7	52.9
Loss, %	2.3	0.1	0.0	0.4	0.8	5.0

NOTE:—*Two treatments of four hours each. Catalyst, 5% MoO_3 (by weight).*

tetralin. On the other hand, no difference in rate of reaction was found in the two experiments. It may be suggested that the difference between the results of these pairs of experiments is due to the different composition of the two pitches. The pitch used in Experiments 172 and 175 would be richer in saturated hydrocarbons, and that used in Experiments 173 and 174 would be richer in polynuclear compounds.

From the point of view of continuous operation in the reduction of bitumen and of coal to oils, the conversion of the resistant pitches is of importance. The foregoing results do not offer much hope that such conversion can be accomplished. However, the results are not extensive enough to make a final conclusion possible. Further experiments, in which higher temperatures or cracking catalysts such as aluminium chloride are used, should be carried out in order to determine under what conditions these pitches may be reduced.

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HYDROGENATIONS IN A TETRALIN MEDIUM

II. DESTRUCTIVE HYDROGENATION OF COAL WITH TETRALIN AND WITH A MIXTURE OF RELATED COMPOUNDS AS MEDIA[1]

By E. H. Boomer[2] and J. Edwards[3]

Abstract

A complex mixture of polynuclear hydrocarbons obtained in the pyrolysis of natural gas has been hydrogenated. The original mixture and the product of hydrogenation have been used as suspension media in the hydrogenation of bituminous and domestic coals, and are compared with tetralin as a medium. The original mixture is much less, and the hydrogenated mixture only slightly less, effective than tetralin.

Introduction

In the first of this series of papers (2), the use of tetralin as a medium in destructive hydrogenation processes was discussed, and it was suggested that other substances might serve with similar results. The present paper gives results of experiments in the hydrogenation of coal in which a fluid mixture of aromatic hydrocarbons known as pyrolysis tar was used as suspension medium.

A large body of literature exists on the hydrogenation of aromatic hydrocarbons, including polynuclear compounds such as naphthalene, anthracene and others (8). Hydrogenation proceeds smoothly and rapidly under proper conditions of moderate temperatures and pressures of hydrogen in the presence of a catalyst. Decomposition reactions begin as the temperature approaches some limiting value, usually near 400° C. (9), and the final product contains paraffins, cycloparaffins and hydro-derivatives of polynuclear hydrocarbons. The use of polynuclear hydrocarbons and their hydro-derivatives in destructive hydrogenations has been mentioned frequently in the patent literture (6), but relatively little has been published in detail. The use of naphthalene and tetralin as media in the hydrogenation of Alberta coal has been reported (4, 5). Beuschlein *et al.* (1), in a series of reports, described the use of anthracene and diphenyl as media in the hydrogenation of American coals. He obtained higher percentage conversions with anthracene.

Materials and Apparatus

Two low-rank Alberta coals, Nos. E-305 and J-309, classified in the Canadian system[4] as bituminous and domestic respectively, were used. Analyses of these coals and the method of preparing them for use, which consisted of drying and grinding them in an inert atmosphere, have been given (5). The coals contained 10.1% and 8.8% ash, on a dry basis.

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Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada and the Research Council of Alberta.

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The pyrolysis tar was obtained as a product of the pyrolysis of natural gas at 950° C. (7). This material was a black, fluid, highly complex mixture of aromatic hydrocarbons. Distillation analysis of the material in an A.S.T.M. gasoline apparatus gave the results shown in Table I. Of the large number of hydrocarbons in the material, benzene, toluene, styrene, chrysogen, chrysene and diphenyl methane occur in small amounts and have been identified. Naphthalene and anthracene were present in large amounts, the former constituting about 25%, and the latter 5%, of the mixture. Finely divided solid material, high in carbon and insoluble in all common solvents, was present as a stable suspension to the extent of 9% by weight. On removal of this material the tar became dark brown.

TABLE I

A.S.T.M. DISTILLATION OF PYROLYSIS TAR

10% over at 208	50% over at 309
20% over at 225	60% over at 325
30% over at 244	70% over at 386
40% over at 269	73.5% over at 390

NOTE:—*Initial b.p. 90° C.; barometric reading, 670 mm. of mercury.*

Molybdic oxide, prepared by roasting ammonium molybdate, was employed as a catalyst in all experiments. Commercial electrolytic hydrogen was used as supplied.

The apparatus, an 1800 cc. oscillating autoclave, and the procedure, have been described in detail (3).

Results and Discussion

All percentage data are given on a weight basis and refer either to the total of coal and ash, on a moisture free basis, plus medium, or to the coal and ash, on a moisture free basis, alone. While the solid residue obtained in these experiments was generally more than half inorganic material, consisting of ash and catalyst, the data tabled refer only to the organic portion. In Experiment 186 the data refer of course to pyrolysis tar only. Under the heading "conversion of coal, A M F basis", all losses and gas production have been assigned to the coal and none to the medium. The original weight of medium was subtracted from the total oil yield to give the yield of oil from coal. The procedure is arbitrary and does not give a correct presentation of the conversion of coal to oil. Most of the losses occurred in connection with the liquid products and should be assigned to both coal and medium. A division of the losses is, however, impossible. Gas was also produced through decomposition of the medium, an idea of the amount being given by the results of Experiment 186, but again a division cannot be made. The most accurate data on the conversion of coal for comparative purposes are shown under "per cent solids".

Treatment of the tar alone, Experiment 186, resulted in rapid absorption of hydrogen. The high yield of solid, 9%, does not represent the true coke formation, as about 9% of free carbon was present initially in the pyrolysis

TABLE II

HYDROGENATION OF PYROLYSIS TAR, AND ITS USE AS A SUSPENSION MEDIUM IN THE HYDROGENATION OF COAL

Experiment No.	186	183	188	189	187	155	161
Medium	Pyrolysis tar			Hydrogenated pyrolysis tar		Tetralin	
Coal sample no.		E-305	J-309	E-305	J-309	E-305	J-309
Medium, gm.	505	204	182	190	199	150	150
Coal, gm.	—	191	182	195	199	200	200
Temperature, °C.	425	450	450	450	450	450	450
Average pressures, lb. per sq. in.:—							
Initial, cold	1120	1090	1115	1120	1130	1000	1045
Maximum, hot	2425	2720	3080	2740	3340	2570	2950
Final, cold	480	435	500	505	500	510	585
Pressure change	−640	−655	−615	−615	−630	−490	−460
Hydrogen absorbed, % AMF coal	2.2	4.1	4 2	3 8	3.7	3.4	3.4
Gas produced, l. per kg. AMF coal	47.0	118	102	115	123	85.0	94.3
Hydrogen in off-gas, % by volume	70.0	44.3	53.9	54 3	48.2	72.0	71.5
Yields, basis AMF coal plus medium							
Liquids, %	85.9	61.2	71.5	77.9	69.0	75.7	72.0
Solids, %	9.0	19.9	10.3	6.3	8.2	7.1	1.8
Charcoal absorber, %	0.8	3.2	2 8	2.8	3.2	4.1	4.2
Gases, %	3.3	10.3	10 5	10.8	12.5	8.7	13.7
Losses, %	1.0	5.4	4.9	2.2	7.1	4.4	7.7
Conversion of coal, AMF basis							
Solids, %		43.4	21.2	13.4	17.5	13.0	3.3
Oils, %		13.8	32.1	49.5	22.8	52.6	41.5
Water, %		1.4	8.6	4 2	11.9	2.8	8.5
Charcoal absorber, %		7.0	5.9	5.8	6.7	7.5	7.7
Gases, %		22.6	22.0	22.5	26.2	16.0	25.0
Losses, %		11.8	10.2	4 6	14.9	8.1	14.0
Distillation of total liquids							
Over at 175° C., %	2.0	4.5	9.6	8.4	11.2	5.3	10.2
Over at 225° C., %	27.3	29.2	32.2	32.9	33.5	55.5	59.8
Over at 300° C., %	50.5	49.8	49 3	49.0	53.0	67.0	71.3
Pitch, %	48.4	49.1	45.0	48.4	37.8	30.6	22.3
Water, %	0 0	1.1	5.7	2.6	8.3	2.0	6.4
Loss, %	1.1	0.0	0.0	0.0	1.0	0.4	0.0

NOTE:—*Two treatments of four hours each. Catalyst, 5% MoO_3.*

tar. It may be concluded that coke formation was really negligible. The distillation curve of the oil recovered was similar to that of the original tar. The oil was, however, much less viscous than the tar and of more pleasant odor. On distillation, about 14% of the oil came over between 200 and 205° C. at a pressure of 700 mm. of mercury. This fraction would be largely tetralin. No naphthalene crystallized from the fractions 210–215° C. and 215–220° C. This oil, containing probably, paraffins, cycloparaffins and hydro-derivatives of polynuclear hydrocarbons, was used directly as medium in Experiments 187 and 189 on coal.

The pressure-time curves, for both treatments, with temperatures taken every half hour, are shown in Fig. 1. Even after four hours the pressure was still falling slowly during the second treatment, indicating that hydrogenation was still incomplete. As is generally true, the maximum pressure was less and the rate of pressure drop was greater in the first treatment than in the second.

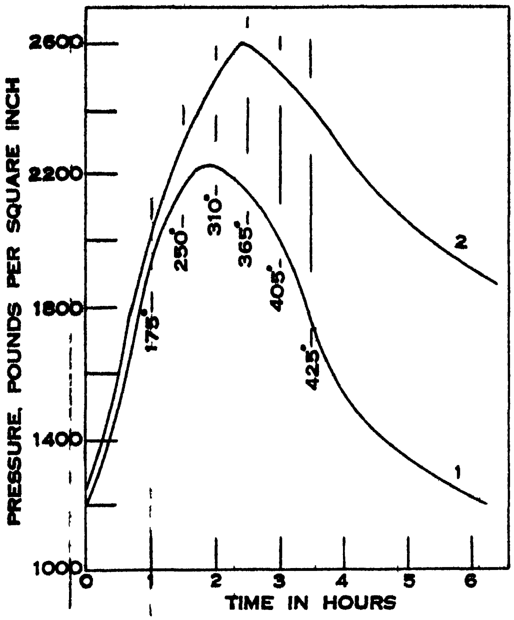

FIG. 1. *Experiment 186. Pressure-time relations with temperatures for both cycles in the hydrogenation of pyrolysis tar.*

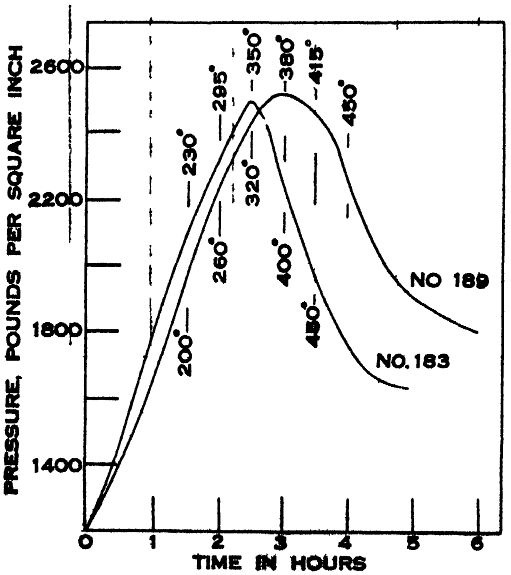

FIG. 2. *Experiments 183 and 189. Pressure-time relations for the first cycles in the hydrogenation of coal in pyrolysis tar. Bituminous coal.*

In Experiment 183, pyrolysis tar was used as medium with bituminous coal, and a fair conversion obtained. The conversion of coal to liquids and gases, plus the losses, 56 6%, while much less than that found with hydrogenated tar or tetralin, is comparable with the conversion of 54 2% obtained with a liquid petrolatum medium (5). It is believed that the low conversion is due to the inability of bituminous coal to compete with pyrolysis tar for a limited supply of hydrogen. The use of hydrogenated tar as medium, as tabled under Experiment 189, gave results directly comparable to those obtained with tetralin in Experiment 155. It should be pointed out, however, that the ratio of hydrogenated tar to coal was 1 0, while that of tetralin to coal was only 0 75. In addition, a better and lighter oil was obtained in Experiment 155. The higher gas yield, higher hydrogen absorption and lower hydrogen content of the off-gas in the presence of tar or hydrogenated tar may be attributed to deficiencies of the media as compared with tetralin.

The pressure-time-temperature data for the first treatments in Experiments 183 and 189 are shown in Fig. 2. The unsaturated nature of the pyrolysis tar is reflected in the lower temperature at which reaction begins and the greater rate of pressure drop in Experiment 183. Except for a more rapid pressure drop, the curve for Experiment 189 is similar to the corresponding curve for Experiment 155. The initial reaction temperature and reaction rate are related to the degree of unsaturation of the suspension medium.

The behavior of domestic coal, No. J-309, in Experiments 187 and 188 indicates again that pyrolysis tar, particularly when hydrogenated, is a satisfactory suspension medium. In general, the relations among the three media in Experiments 161, 187 and 188 are much the same as for Experiments 155, 183 and 189, when account is taken of the difference between the coals. Domestic coal is more easily hydrogenated than bituminous coals, although the oil yield may be smaller because of the large amount of water and gas formed. The high conversion of coal to liquids and gases obtained with pyrolysis tar, plus losses, of 78.8%, may be compared with 68.1% obtained with liquid petrolatum (5). This high figure would suggest that domestic coal can compete with pyrolysis tar for hydrogen rather more successfully than can bituminous coal. Hydrogenated tar is definitely better as a medium although not as effective as tetralin. However, it is believed that pyrolysis tar can be hydrogenated so as to produce a product substantially as effective as tetralin.

Fig. 3 presents the pressure-time-temperature data of the first treatments of Experiments 187 and 188. The low temperature at which reaction began and the low maximum pressure in Experiment 188 show the unsaturated nature of the medium. The relatively short time required for the pressure to become constant may be attributed to the reactivity of domestic coal.

In conclusion, it may be said that pyrolysis tar can be hydrogenated readily, and the resulting oil shows promise as an effective suspension medium in the reduction of coal to oils. The good results obtained with a medium of hydrogenated tar are due to the presence of tetralin and other hydro-derivatives of polynuclear hydrocarbons. The results are of some practical value in connection with the utilization of waste natural gas.

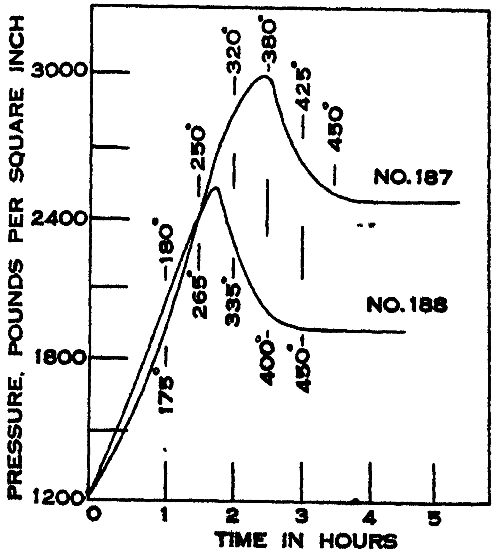

FIG. 3. *Experiments 187 and 188. Pressure-time relations for the first cycles in the hydrogenation of coal in pyrolysis tar. Domestic coal.*

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HYDROGENATIONS IN A TETRALIN MEDIUM

III. DESTRUCTIVE HYDROGENATION OF CELLULOSE AND WOOD[1]

By E. H. Boomer[2], G. H. Argue[3] and J. Edwards[4]

Abstract

The destructive hydrogenation of cotton wool cellulose and fir wood sawdust in a tetralin medium was investigated. When it is present in sufficient excess, tetralin promotes the complete conversion of cellulose and wood to liquids and gases in the absence of a catalyst. The tetralin acts as a hydrogen carrier in fulfilling the function of a catalyst.

Introduction

Continuing this series on the value of tetralin as a suspension medium in destructive hydrogenations (2), the present paper presents the results of some experiments with cotton wool cellulose and fir wood sawdust.

The hydrogenation of cellulose and wood has attracted the attention of many investigators. Palmer (11, 12), in a study of the distillation of birch wood in which phosphoric acid was used as catalyst, observed increased yields of methanol at moderate pressures (60 to 150 lb. per sq. in.). Hawley (9) failed to confirm the finding with regard to the value of phosphoric acid, but found improved yields with lime, calcium and sodium carbonate. Bergius (1) subjected cellulose to thermal decomposition in a closed vessel under the pressure of the autogenous gases. The coal-like substance obtained was hydrogenated and a small quantity of oil resembling petroleum was formed. Bowen, Shatwell and Nash (5) found that at 420–440° C. there was no appreciable production of liquid from cotton cellulose in the presence of hydrogen at 40 atm. Nickel catalyzed the production of oils, however, but iron and vanadium did not. Bowen and Nash (4) found a nickel and alumina catalyst particularly effective, and that more than 80% of the cellulose was converted to liquids and gases. Methane was present in the gases. Fierz-David and Hannig (6), in their investigations on cellulose and wood, found that distillation was not affected by the presence of hydrogen at a pressure of 300 atm. unless a catalyst, nickel, were present. Copper was less effective, and iron, of little effect. In the presence of nickel, the conversion to gases and liquids was almost quantitative, the liquids containing alcohols, aldehydes, ketones, acids, furans and phenols in addition to water. In general, it has been found that carbon dioxide is the chief gaseous product at low decomposition temperatures, carbon monoxide, hydrogen and methane appearing at higher tem-

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peratures. Waterman and Perquin (13) have confirmed the observations that cellulose is not hydrogenated to oils in the absence of a catalyst, although a 38% yield of a viscous yellow oil was obtained by vacuum distillation of cellulose. The use of a suspension medium of Borneo petroleum resulted in less coke and more hydrocarbons being formed. Frolich *et al.* (7) reported on the treatment of sulphite pulp cellulose and wood under pressure of hydrogen, nitrogen and autogenous gases. More than 90% of the wood was converted to liquids and gases in the presence of nickel. Cellulose was almost completely converted by hydrogenation in the presence of nickel, but the use of nitrogen with nickel resulted in the production of 14% of coke. Lindblad, using a variety of catalysts in an extensive investigation on the hydrogenation of wood (10), found that nickel and cobalt were effective in promoting conversion of wood to tar at 250° C. Methane was formed at higher temperatures. Hydrogenation of sawdust impregnated with cobalt sulphide at 350° C. resulted in a 40% yield of oils, and a large hydrogen absorption (approximately 5%). The use of sulphite liquor as suspension medium and ferrous sulphide as catalyst yielded excellent results, *e.g.*, conversions of 58% to oils and 12.4% to water, a residue of 13%, and a hydrogen absorption of 5.5% by weight of the wood.

The present paper describes experiments in which tetralin was used as suspension medium without any catalyst other than the walls of the reactor, and which showed high conversions of cellulose and wood to liquids and gases. The work is of a preliminary nature and demonstrates chiefly the effectiveness of tetralin as a medium.

Materials and Apparatus

The cellulose used was a commercial grade of absorbent cotton. British Columbia fir wood sawdust containing 0.31% ash and 5.2% moisture was dried at 110° C. and used without further treatment. Tetralin of a practical grade, b.p. 204–206° C., and commercial electrolytic hydrogen were employed.

Two types of apparatus have been used. The results in Table I were obtained on small amounts of materials in a small vertical autoclave of 180 cc. capacity and fitted with a glass thimble as liner. The materials were introduced into the autoclave in the glass thimble, closure was effected, the apparatus flushed with hydrogen and the hydrogen pressure raised to 1000 lb. per sq. in. The autoclave and attached recording pressure gauge were isolated from the rest of the apparatus by means of valves, and the temperature was raised to the desired operating value as rapidly as possible. The temperature was kept constant by means of an automatic controller governed by a thermocouple. After a chosen reaction time, the autoclave was cooled to room temperature, the gases were drawn off and analyzed, and the autoclave was opened for removal of liquid and solid products.

The experiments listed in Table II were carried out with larger samples of wood in an 1800 cc. oscillating autoclave already described (3).

Results and Discussion

The results shown in Table I were obtained with the use of relatively large amounts of tetralin as compared to those of cellulose and wood. Certain characteristics were common to all these experiments. The pressure rose with the temperature to a maximum value, as tabled, and remained constant thereafter while the temperature was constant. The water recovered was in all cases strongly acid, and the odor of the light oil was similar to that of aldehydes. The initial boiling point of the liquid was always lower than 50° C. The solid residues adhered very firmly to the glass container and could not be weighed with any degree of accuracy. In Table I, "Trace", as applied to the solid residue, means that it consisted of a black film of a tarry nature on the glass surface. By "Small" is meant this same black film with a few grains of imbedded coke. "Large" indicates that the solid residue appeared to be unchanged starting material, except that the color was black.

TABLE I

HYDROGENATION OF CELLULOSE AND WOOD IN TETRALIN AT 350° C.

	Cellulose			Wood		
Experiment no.	5	7	8	9	10	11
Material, gm.	8	8	12	18.6	15.2	15.2
Tetralin, gm.	48.6	58.3	0	58.3	58.3	0
Gas, 1000 lb. per sq. in.	H_2	CH_4	H_2	H_2	CH_4	H_2
Maximum pressure, hot, lb. per sq. in.	2800	4150	3600	3850	4050	2275
Solid residue, gm.	Trace	Small	Large	Trace	2.5	7.8
Liquid recovered, cc.	50	60	1.0	69	65	0.3
Distillation of liquid						
Water, cc.	1.5	2.0	Trace	4.1	2.7	Trace
Oil to 200° C., cc.	2.5	1.5	Trace	2.5	1.5	Trace
Pitch, cc.	5.0	3.2	Trace	12.4	5.0	Trace
Naphthalene, cc.	—	2.0	—	—	2.0	—
Gas analysis, not including added gas						
CO_2, %	47.6	32.0	59.4	51.4	48.1	48.4
CO, %	18.7	22.2	13.0	12.2	32.3	11.5
Olefines, %	1.5	2.6	0.0	1.1	5.3	1.6
CH_4, %	24.2	—	14.5	28.6	—	38.5
C_2H_6, %	7.8	—	13.0	6.6	—	0.0
H_2, %	—	43.0	—	—	14.3	—
Hydrogen in off-gas, %	87.6	6.6	85.8	53.0	1.9	74.9
Hydrocarbons in off-gas, %	—	78.9	—	—	84.8	—

Preliminary experiments were carried out with cellulose at 200, 250 and 300° C. At 200° C. reaction was very slight and no liquid products were formed. The cellulose was apparently changed only in color. Carbon dioxide, carbon monoxide and methane appeared in small amounts in the off-gas. At 250° C. reaction was more evident, but the solid residue was still large, of the same form as the original cellulose, and was black and slightly charred. Distillation of the liquid through a micro-column yielded traces of acidic water, light oil and 3 gm. of a high boiling tar. At 300° C. dissolution of the cellulose was almost complete, leaving only a small residue. On distillation of the liquid, 0.5 gm. of light oil, 0.2 gm. of water and 2.5 gm. of tar were recovered from a 40 cc. sample of the liquid in the autoclave.

Experiments 5, 7 and 8 were comparative experiments carried out to demonstrate that tetralin was largely responsible for dissolution of the cellulose. In Experiment 5, with hydrogen and tetralin, the cellulose disappeared completely, leaving only a black tar film on the glass. In Experiment 7 the hydrogen was replaced by natural gas, largely methane. While the cellulose was not completely dissolved, the residue was very small and not recoverable. The identification of naphthalene in the liquid recovered showed that some dehydrogenation of tetralin had taken place. In Experiment 8 it was demonstrated that tetralin is essential to the reduction of cellulose. In this experiment the cellulose was charred but retained its original physical form. The liquid residue appeared to be largely water.

The gas analyses are interesting in showing that methane and ethane together form the major portion of the gas. The analyses are based on the off-gas less the original gas (hydrogen in the case of Experiments 5 and 8 and natural gas in Experiment 7). Experiment 7 shows that hydrogen is a product of the reaction, although it is unknown to what extent tetralin is the source. Hall (8) states that tetralin becomes unstable at temperatures higher than 400° C., but he did not find naphthalene to be completely converted to tetralin at 350° C.

Experiments 9, 10 and 11 on wood constituted a series corresponding to that on cellulose, and demonstrate conclusively that tetralin is required for the dissolution of wood. Except for the change in color to black, the sample of wood used in Experiment 11 was apparently unaltered. A trace of liquid was formed and carbon dioxide, carbon monoxide and methane were produced, showing that some reaction occurred. As with cellulose, tetralin alone was able to reduce wood to liquids and gases rather effectively, naphthalene being produced in the process.

It is evident that tetralin is an efficient medium in which to carry out the hydrogenation of cellulose and wood. In view of the fact that a catalyst is necessary, as demonstrated in previous investigations already discussed, and the results found in the present work in which no catalyst was used, it appears that tetralin also fulfils the function of a catalyst.

In Table II are shown the results of three experiments with dry fir sawdust on a larger scale than those reported in Table I. Apart from the larger scale, the essential difference between these experiments and those listed in Table I lies in the tetralin-wood ratio. Here the ratio is 1 or 1.2 to 1, compared to about 3 or 4 to 1 in Experiments 9 and 10.

The material removed from the autoclave contained much volatile material, and losses occurred before the weight could be determined. After it was weighed, the material was filtered, and the solid residue washed with ether, dried and weighed. It was considered that this solid material, coke-like in appearance, was formed solely from the wood. The losses were due largely to evaporation of the volatile products of the reactions and only in small part to losses of solvent. For this reason the conversion figures in Table II show all the losses combined with the figures for oil and gas. The oil was distilled until the temperature was 50° C. and the distillate, largely ether, was discarded. No doubt some volatile products of the reaction were contained in this ether fraction. The remaining oil was fractionated in a 14-in. packed column, and the results are tabled. Assuming the fraction 200-206° C. to be mostly tetralin, the recovery of tetralin is quite high, more than 80% in Experiments 16 and 18 and more than 90% in Experiment 17.

TABLE II

HYDROGENATION OF WOOD IN TETRALIN

Experiment no.	16	17	18
Tetralin, gm.	180	198	148
Wood, gm.	152	163	149
Temperature, °C.	325	350	325–375
Pressures, lb. per sq. in.			
Initial, cold	1200	1220	1140
Maximum, hot	3435	3740	3475
Final, cold	1175	1205	1140
Hydrogen absorbed, % weight of wood	2.5	3.3	3.7
Gas produced, less H_2, litres	5.3	6.8	10.9
Yields, basis charge,			
Solids, %	34.3	20.2	23.9
Liquids, %	56.9	68.7	65.0
Gases, %	1.1	1.2	1.3
Loss, %	7.7	9.9	9.8
Conversion of wood,			
Solids, %	75.0	44.8	47.7
Oil, gas, and loss, %	16.5	46.0	42.2
Water, %	8.5	9.2	10.1
Distillation of liquid			
Water, %	6.9	8.7	7.8
Oil to 175° C., %	1.7	2.3	1.7
Oil to 225° C., less 200–206° C. fraction, %	5.8	12.7	13.1
Oil, 200-206° C., %	80.4	68.4	64.3
Pitch, above 225° C.	6.9	10.2	14.8
Gas analysis			
CO_2, %	7.0	8.0	4.3
Olefines, %	0.0	0.4	0.0
H_2, %	89.2	81.3	90.6
CO, %	0.9	1.3	0.6
CH_4, %	2.9	7.3	3.3

Experiments 16 and 17 were single treatments of one and two hours' duration respectively, while Experiment 18 was a double treatment experiment at 325° C. in the first and 375° C. in the second treatment. The data on conversions are based on the solid residue and water recovered. The yield of oil and gas is a much less certain quantity, including, as stated above, all the losses consequent to handling the material.

The conversion at 325° C. is small but probably due to hydrogenation more than to thermal decomposition. The absorption of hydrogen is large enough to suggest that reduction of the wood occurred, although some of the hydrogen may have combined with tetralin.

Experiment 17 is directly comparable with Experiment 9, Table I, in that both were carried out at 350° C. The difference in conversion may be attributed to the difference in relative amounts of tetralin. It is suggested that the large excess of tetralin in Experiment 9 permits very rapid hydrogenation of the primary products of thermal decomposition of wood. In the absence of a large excess of tetralin, thermal decomposition may proceed to coke formation because of a slower rate of hydrogenation.

In Experiment 18 the wood was treated first at 325° C., and second, with a fresh supply of hydrogen at 375° C. in an endeavor to increase the conversion. It was apparent that the results were slightly less satisfactory than those obtained at 350° C. with one treatment. There were no great differences in the results of Experiments 17 and 18, although a more extensive reaction is suggested by the higher hydrogen absorption and water production in the latter.

The results of these experiments indicate that wood can be successfully hydrogenated in the presence of tetralin without a catalyst. The temperature should be greater than 325° C. and preferably about 350° C. It is essential for complete reduction to oils and gas that the tetralin be present in relatively large excess, not more than 3 parts of tetralin to 1 of wood, but certainly more than 1.2 to 1.

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HYDROGENATIONS IN A TETRALIN MEDIUM

IV. DESTRUCTIVE HYDROGENATION OF GRAIN SCREENINGS[1]

By E. H. Boomer[2] and J. Edwards[3]

Abstract

The destructive hydrogenation of grain screenings in a tetralin medium has been investigated. With an excess of tetralin, at least 3 to 1 by weight, more than 50% of the screenings can be reduced to oils and about 15% to solid residue. Catalysts are effective by virtue of the fact that they greatly increase the rate of reaction, and also increase the production of hydrocarbon gases at the expense of carbon dioxide

Introduction

In a previous paper of this series (1), it was shown that tetralin is a most efficient suspension medium in the hydrogenation of cellulose and wood. In view of the general similarity of the properties of grain screenings, cellulose and wood, it was suggested by Dr. W. H. Cook* that an investigation of the process as applied to screenings would be of interest.

Grain screenings consist of a mixture of weed seeds, grain, seed coats and chaff, and accumulate in large amounts at the elevators in Fort William and Port Arthur each year, and their disposal presents a serious problem. The screenings consist largely of cellulose and lignin, but contain in addition considerable amounts of vegetable oil by virtue of their seed content. A market exists for part of the material as stock feed, and various suggestions have been made regarding the use of the surplus as fuel or as a source of vegetable oils. The present paper does not pretend to suggest an outlet for grain screenings; it is an account of a preliminary investigation that may be of some possible future interest.

Materials and Apparatus

Grain screenings were supplied as collected and in four different fractions. A description of these appears in Table I together with that of a sixth material, which consisted of equal parts of the solid residues from the hydrogenation of Samples 4 and 5.

Sample 1, whole grain screenings, was made up of equal parts of Samples 2 to 5. Any one sample was not particularly free from the constituents of the other samples, but was predominantly as described.

Tetralin of a practical grade, b.p. 204–206° C., was used throughout, and the hydrogen was the usual electrolytic grade.

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TABLE I

MATERIALS

Sample no.	Dry matter as % of wet weight	Description
1	91.4	Whole grain screenings
2	90.8	Black seeds, lamb's-quarter and small seeds, etc.
3	91.4	Refuse screenings, very fine material, seed coats and chaff
4	91.3	Refuse screenings, coarser than No. 3
5	91.5	Ragweed screenings, grain, large material
6	100.0	Solid residues from hydrogenation of Nos. 4 and 5 in equal parts.

Two types of apparatus and procedure were used, the first permitting batch operation, and the second, semi-continuous operation. They will be described in connection with the results.

Results and Discussion

The data obtained in this work are given in Tables II and III. Table II presents results obtained in preliminary work, in which a batch method was used with the different samples of screenings. Table III presents results obtained with dry whole screenings, Sample 1, with a semi-continuous method of operation and larger relative amounts of tetralin.

Batch Hydrogenations

The apparatus and procedure have been described in all their essentials previously (2). Briefly, the screenings and tetralin were weighed, introduced into an 1800 cc., oscillating autoclave, hydrogen was admitted and the temperature raised to that desired. After two hours at constant temperature, the autoclave was cooled, the gas drawn off, metered and analyzed, and the autoclave opened. The material in the autoclave was removed as completely and expeditiously as possible, weighed and filtered. The residue on the filter was washed with ether until free from oil, dried and weighed. The ether-oil solution was heated on a water bath, and the ether taken off together with some of the volatile constituents of the oil.

The data given in Table II are all on a weight percentage basis. In calculating the conversions of screenings to solid, liquid and gas, all the losses were assigned to the screenings. The original weight of tetralin was subtracted from the weight of liquids recovered. The high and variable losses were due to difficulties in handling the material and inability to prevent losses by evaporation during the process of emptying the autoclave. There is no doubt that part of the loss should be assigned to the tetralin. The yields of gas and solid residue are the most trustworthy data, and the sum of the oil yield and loss will give a better measure of the conversion of screenings to oil than the figures tabled. The gas production, given in litres at a pressure of 760 mm. of mercury and 0° C., does not represent the true value, inasmuch as the hydrogen has not been included. It is highly probable that hydrogen is produced in the reaction to some extent. The recovered oil was fractionated in a 14 in. packed column, and the results are tabulated as percentages of the total liquid recovered, including water. These figures do not include the more volatile products lost during the ether treatment. The initial boiling point of the crude oil always lay between 50° and 60° C., while the recovered oil, as entered in the table, showed initial boiling points between 76° and 80° C. The data on the 200-206° C. fraction have been tabulated separately to indicate roughly the tetralin content of the oil. Assuming this fraction to consist substantially of tetralin, more than 90% of the initial quantity was recovered in experiments on Samples 1, 4 and 6.

TABLE II

BATCH HYDROGENATION OF GRAIN SCREENINGS IN TETRALIN WITHOUT A CATALYST

Sample no.	1	2	3	4	5	6
Screenings, gm.	367	345	267	295	311	245
Tetralin, gm.	236	210	200	211	244	196
Temperature, °C.	350	250–350	325	300	325	350
Pressures, lb. per sq. in.		(1)–(2)				
Initial, cold	1110	1170–1100	935	990	1115	1095
Maximum, hot	4920	2960–4350	3420	2560	4040	2390
Final, cold	1235	1170–1100	1035	755	1205	785
Conversion of screenings						
Solids, %	39.5	51.6	55.8	62.0	69.5	73.5
Liquids, %	31.6	21.4	19.9	21.4	8.4	16.3
Gases, %	7.0	4.2	4.7	4.6	5.0	0.7
Losses, %	21.9	22.8	19.6	12.0	17.1	9.5
Gas yield, less hydrogen, litres	35.8	17.9–10.0	18.6	21.9	21.9	3.4
Gas analysis:—						
CO_2, %	26.2	19.1–11.7	21.7	27.6	20.2	4.6
CO, %	1.0	0.5– 0.6	1.2	1.0	0.5	0.5
H_2, %	60.5	76.1–82.6	72.0	64.3	73.9	91.2
CH_4, %	10.5	2.1– 4.7	5.3	4.8	5.2	3.6
C_2H_6, %	1.3	0.0– 0.0	0.0	0.9	0.0	0.0
Distillation of liquid recovered:						
Water, %	9.6	13.7	9.0	3.9	9.9	0.9
Oil, less 200–206° C. fraction:						
Over at 175° C., %	1.9	2.1	0.9	0.4	4.0	1.7
Over at 225° C., %	5.3	6.6	6.3	5.7	10.3	4.7
Over at 300° C., %	8.9	13.3	12.4	10.5	13.9	11.1
200–206° fraction, %	62.7	53.1	63.3	71.6	55.1	76.0
Pitch, %	18.1	19.9	14.9	12.7	21.1	12.0
Loss, %	0.7	0.0	0.4	1.3	0.0	0.0

NOTE:—(1) *First treatment.* (2) *Second treatment.*

Limited amounts of each sample, except No. 1, were available and one experiment only was carried out with each. The use of different conditions for each sample was justified on the assumption that the various fractions would behave nearly alike. Only one constituent, black seeds, showed a definite difference from the others in its resistance to destruction. While all other constituents were destroyed or formed amorphous coke at 300 to 325° C., black seeds retained their outward physical form at 350° C.

The gas yields were low in all cases and the principal constituent of the gas was carbon dioxide. There were lesser amounts of paraffin hydrocarbons. In the experiment with Sample 2, in which two treatments were used, the gas analyses show that the bulk of the carbon dioxide appeared in the first treatment at 250° C. Examination of the pressure-time and pressure-temperature records of all these experiments showed a rapid exothermic reaction near 250° C., during which the pressure rapidly increased 400 to 500 lb. per sq. in. This effect was missing in the second treatment of Sample 2 at 350° C. and in the experiment on Sample 6, in which previously hydrogenated residues were used. The conclusion is that this reaction is accompanied by the release of carbon dioxide.

The amount of water formed was large in all experiments except those in which Samples 4 and 6 were used. In the first case, the low temperature of 300° C. may account for the result, and in the second, the water was probably eliminated in the previous treatments. The low yield of water at 300° C. suggests that the reaction responsible occurs at a temperature considerably higher than that required for the production of carbon dioxide. The high yield obtained in the experiment with Sample 2 may be attributed to the double treatment employed. The water was strongly acidic in all cases, and contained considerable amounts of soluble low-boiling material.

The oils were highly odorous, light yellow and acid in reaction. They were very unstable and darkened rapidly on standing. On distillation, cracking became extensive at or above 200° C. No ultimate analyses of the oils or other products were carried out. However, the oils contained without doubt considerable oxygen. Only about 20% of the oxygen, 5% of the carbon and 10% of the hydrogen content of the screenings were converted to gas and water.

The yield of solid residues was higher than expected, and the result suggests the use of a larger relative amount of tetralin. The best temperature appears to be 350° C. or as an alternative, treatment at 300–325° C. followed by hydrogenation of the residue at 350° C., as with sample No. 6. The double treatment method used with Sample 2 is not effective when compared with a 55.3% over-all conversion to gas and liquid obtained with Samples 4, 5 and 6 in combination.

Semi-continuous Hydrogenations

The apparatus used is shown in Fig. 1. Hydrogen from storage entered through the check valve, *A*, and stop valve, *S*, to a surge bottle, *B*. A pressure gage, *C*, indicated the pressure in the system. Connection was made to the autoclave, *D*, through the valve *L*. The autoclave, of 400 cc. capacity, was placed vertically in a split electric furnace, *E*, and was fitted at the top end with a column, *F*, 12 in. long and ½ in. in diameter. The temperature of the autoclave was determined by means of a thermocouple inserted in a well drilled in the wall of the autoclave. Temperature control was automatic to within 5° C. The column, *F*, was heated by burners operating in an asbestos jacket, and the temperature was read on the thermometer, *R*. Manual temperature control was obtained by adjusting the burners. A water-cooled pressure condenser, *G*, was connected to the expansion valve, *H*, in a heated oil bath, *N*. The expanded gases were passed through a condenser in the ice bath *J*, a flow-meter *P* and wet test meter *K*, to a gas-holder.

Weighed quantities of screenings and tetralin were placed in the autoclave, closure was effected, hydrogen admitted until the pressure was about 1000 lb. per sq. in., and the heat turned on. When the temperature was 200° C., hydrogen was admitted at the storage pressure shown in the table, and valves *S* and *L* were left open. The expansion valve was opened and adjusted to give the desired rate of flow. The column, *F*, was heated rapidly at the top to the desired temperature. After some definite time, heating was discontinued, valve *L* closed, and the autoclave was cooled rapidly by opening the furnace. The contents of the pressure condenser was removed through valve *M* and weighed together with the contents of the ice condenser, *J*. The contents of the autoclave was removed as completely as possible, weighed and filtered. The residue in the filter was washed with ether, dried and weighed. The ether washings were heated on a water bath, and the residual oil added to the condensates and filtered oil. A slight loss of volatile material occurred during removal of the ether. The oily material was fractionated as described previously and the aqueous layer fractionated in a micro-distilling column. Both the aqueous layer and oil were strongly acid, and their initial boiling points were between 50° and 60° C. Between 20 and 30% of the aqueous layer boiled below 95° C.

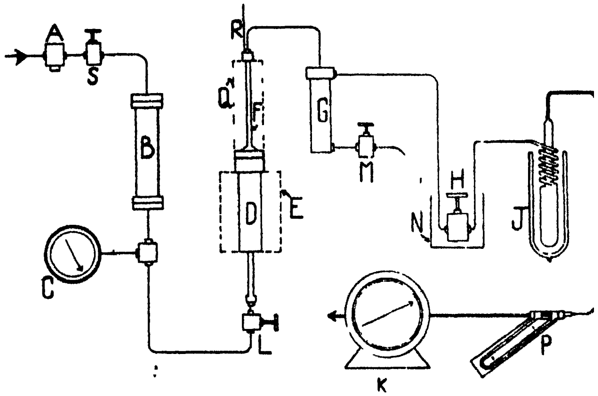

FIG. 1. *Apparatus for hydrogenation in a stream of hydrogen.*

Three experiments, Nos. 57 and 58 on screenings and No. 59 on the combined pitches from Experiments 51 to 58, were carried out with catalysts. In No. 57 a highly active methanol catalyst, consisting of equimolar parts of zinc oxide, copper oxide and aluminium oxide, was used. In Experiments 58 and 59 molybdic oxide was employed. Ten grams of the powdered catalyst was used in each case.

Reference to Table III shows that the losses were high in many cases. The losses were due principally to inability to recover all the contents of the autoclave, and the fact that some of the volatile materials passed through the condenser. The conversions of screenings to solids and water given in Table III are, as a consequence, somewhat low, but the principal losses were associated with the oil. All the loss found was assigned to the screenings, although there is no doubt that part should have been assigned to the medium.

TABLE III

SEMI-CONTINUOUS HYDROGENATION OF GRAIN SCREENINGS IN TETRALIN

Experiment no.	52	53	54	55	56	57	58	59
Tetralin, gm.	60	148	150	150	150	150	150	150
Screenings, gm.	45	50	50	50	50	50	50	50
Temp. of autoclave, °C.	350	350	375	400	400	400	400	425
Temp. of column, °C.	64	65	67	220	215	215	220	235
Operating pressure, lb. /sq. in.	2600	2450	2300	2150	2850	2650	2300	3150
Hydrogen flow, cc./min.	130	120	130	125	180	180	180	185
Time at temperature, min.	40	20	60	60	120	60	60	40
Total off-gas, litres	53.6	15.8	47.2	26.4	46.1	23.0	25.0	19.0
Yields, basis screenings plus tetralin:—								
To solids, %	23.8	12.1	8.0	6.0	4.0	3.5	4.0	0.5
To liquids, %	69.8	83.8	83.0	83.5	84.5	81.5	83.5	92.5
To gases, %	0.7	0.5	0.8	1.1	1.1	0.7	0.7	0.2
To losses, %	5.7	3.4	8.3	9.4	10.4	14.3	11.5	6.8
Conversion of screenings:—								
To solids, %	55.6	48.0	32.0	24.0	16.0	14.0	16.0	1.7
To water layer, %	18.5	23.0	24.0	20.0	24.0	24.0	24.0	3.3
To gas, %	1.6	2.0	3.2	4.4	4.4	2.8	2.8	0.8
To oils, %	11.0	13.5	7.6	14.0	14.0	2.2	11.2	67.0
To losses, %	13.3	13.5	33.2	37.6	41.6	57.0	46.0	27.2
Distillation of liquids:—								
Water layer, %	11.4	7.8	7.7	6.3	7.3	8.3	8.4	1.0
Oil, less 200–206° C. fraction:—								
Over at 175° C., %	1.0	1.3	2.0	3.1	2.8	2.8	1.4	0.5
Over at 225° C., %	5.0	8.5	4.2	5.6	5.6	3.4	4.0	3.2
200–206° C. fraction, %	76.3	76.8	78.7	78.7	77.0	77.3	77.8	74.4
Pitch, %	7.3	6.9	9.4	9.4	10.1	11.0	9.8	21.4
% of water boiling below 95° C.	22.5	25.6	24.0	28.0	30.0	18.0	23.0	—

NOTES:—*Experiment 57—10 gm. of ZnO-CuO-Al_2O_3 catalyst added to charge. Experiments 58 and 59—10 gm. of MoO_3 added to charge. Experiment 59—pitch residues used in place of screenings.*

The tabled values for conversions to oil are as a result highly inaccurate, and it is probable that the sum of the loss and the quantity of oil gives a more nearly correct figure for the conversion to oils. The figures for "solids" are the most accurate.

The physical form of the most resistant constituent, black seeds, was destroyed only at 400° C. In Experiments 52 and 53, the individual seeds, charred of course but of the original shape, could be picked out of the solid residue. In Experiments 54 and 55 at 375° and 400° C., traces of the seeds were evident, but the solid residue was nearly homogeneous and amorphous. In the other experiments, the residues were completely amorphous, and no seeds or seed coats survived destruction.

The variables are numerous and it is difficult to evaluate their effect from the results of the limited number of experiments carried out. The temperature of the column and the rate of gas flow did not appear to have much effect, except in controlling the amount of material collected in the condensers. As it was desirable to remove the more volatile products rapidly, it was found necessary to keep the column head at a temperature of 200° C. or higher. At lower temperatures very little material came over in the gas stream.

The effect of time, temperature and the ratio of tetralin to screenings is shown best in Experiments 52 to 56. In Experiments 52 and 53, an increase in ratio from 1.3 to 3 more than counteracts a decrease in time from 40 to 20 min. Increasing the temperature slightly from 350° to 375° C. and increasing the time to 60 min. in Experiment 54 caused a pronounced decrease in the amount of solid residue. The same beneficial effect of increasing temperature and time is noticeable in Experiments 55 and 56.

The presence of catalysts in Experiments 57 and 58 is of benefit in reducing the amount of solid residue to the same value obtained in Experiment 56, which lasted twice as long. Both catalysts appear to be equally effective and influence the rate of reaction only.

The oils and water recovered in this series of experiments were very similar in properties to those obtained in batch experiments. The pitch residues left at 225° C. were combined and hydrogenated in Experiment 59. The pitches were reduced to a very stable oil, most of which had the same boiling range as the original pitch. The production of water in Experiment 59 shows that the pitches contained oxygen compounds that could be reduced at 425° C., although they were stable at 400° C.

Gas formation in these experiments was slightly less than that found in batch hydrogenation. This is not an unexpected result, in view of the removal of the reaction products from the autoclave as formed. It was interesting to note that the gas formation was less in the presence of the catalysts. A further effect due to the catalysts, but not indicated in the table, was shown by the gas composition, the amount of carbon dioxide produced being less and that of the hydrocarbons being greater, the latter forming the principal constituent of the gas.

In conclusion, it may be said that grain screenings can be reduced very largely to liquids and gases in the presence of an excess of tetralin. About 15% of the screenings remain as solids, and probably 50% or more can be obtained as oils by operation at 400° C. with a 3 to 1 ratio of tetralin to screenings. Comparing the results with similar experiments on cellulose and wood (1), it may be stated that grain screenings are definitely more resistant to reduction under the conditions used. It is highly probable that more effective reduction with the formation of little or no solid residue could be obtained after some further investigation.

Acknowledgments

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STUDIES OF CARBON BLACK

I. A NEW PROCESS FOR THE PRODUCTION OF CARBON BLACK BY THERMAL DECOMPOSITION OF HYDROCARBON GASES[1]

BY L. M. PIDGEON[2]

Abstract

A method is described whereby carbon black is produced from hydrocarbon gases such as methane or propane-butane by thermal decomposition of these gases in a heated tube. The essential feature of the process is the use of a porous refractory tube through which a certain amount of inert gas is allowed to pass. By this means the reacting gas is unable to touch the walls of the system, and deposition of carbon thereon is prevented. Yields as high as 60% of the carbon in the gas, corresponding to 65 lb. per thousand cubic feet, have been obtained from a 70–30 propane-butane mixture, and 19 lb. from methane. The carbon black produced by this process is similar to the "soft" blacks in that it has a high density, low sorptive power, it accelerates the cure in a rubber stock and gives similar resistance to aging and abrasion. It imparts greater stiffness to a rubber stock, however, and in many ways occupies a position between the channel and the "soft" blacks.

Introduction

Carbon black has become one of the most important pigments employed in the rubber industry, as no other substance has been found that will impart similar abrasion resistance to rubber. In spite of the large amounts that are used, the method of production has undergone very little alteration since its inception, and to-day is one of the most wasteful processes known to chemical industry. Most of this carbon black is produced by the impingement of a luminous gas flame on a moving iron plate or other surface, the most common form being a channel section. Subsequent papers in this series will deal with experiments on the preparation of carbon black by the channel process and the relation between the controllable variables and their effect on the properties of the black.

The flame impingement process results in the recovery of not more than 4% of the carbon content of the gas. Such poor yields may be tolerated only where large amounts of natural gas are available, and while there has been the opposite of shortage up to the present time it is quite clear that the situation cannot continue indefinitely, and even now restrictive measures are contemplated or in operation. Much higher recovery of carbon may be obtained by thermal decomposition of the gases in tubes or retorts, but, so far, the carbon produced is distinctly different in type and has had but limited applications. It seems clear, however, that any advances in the methods of production are most likely to be made in this direction. This paper describes the production of carbon black by thermal decomposition of methane and similar gases under conditions such that 60% of the available carbon is

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[1] *Manuscript received October 28, 1935.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

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recovered. The essential point of the process is the use of a porous reaction tube through which some of the heating gases pass, with the object of preventing deposition of carbon on the walls.

There are no theoretical reasons why a gas such as methane could not be decomposed into its elements in such a manner as to recover all the carbon. The decomposition involves the absorption of some 19,000 calories which may readily be supplied by combustion of the resultant hydrogen. There are a number of practical difficulties, however, that prevent the realization of such yields.

While free energy data indicate that methane is unstable above 575° C. (5), it is known that decomposition is inappreciable below 700°, and even at 1300° in the presence of catalytic surfaces it is incomplete after one hour. The problem therefore becomes one of design. It is necessary to develop an apparatus in which a hydrocarbon gas may be subjected to temperatures in excess of 1300° for a time long enough to disintegrate it into its elements, and in such a manner that the carbon may be recovered in a flocculent condition.

It is also essential that the time of contact shall be as short as possible, since it is known from analogy with the flame process that such a condition is required to produce the fine particles that are responsible for the reinforcement of rubber (1, p. 1042). This limitation necessitates the use of higher temperatures than would be required if thermal decomposition were the only end to be achieved.

These requirements are fulfilled by operation at temperatures so high that a very short contact time is sufficient to disintegrate the molecule into its elements. However, a very serious practical difficulty arises from the fact that the heat necessary to carry on this endothermic reaction must be supplied through the walls of the reaction chamber, which will be the hottest part of the system and upon which the reaction will be most active. Any attempt to produce carbon in a heated tube invariably results in the deposition of a layer of carbon on the walls which, owing to its poor heat conductivity, soon insulates the reaction zone from the source of heat. Furthermore this carbon is deposited in a hard gray, lustrous, condition, and is not useful for the purposes for which carbon black is used.

It is clear that a "wall free" reaction space must be obtained similar to that existing in a flame, in which the heat may be supplied by radiation, since the reacting gas must not touch the walls. A number of methods, several of which have been so successful as to warrant large-scale operation, have been evolved to overcome this difficulty.

In the "Gastex" (2) process parallel gas streams are employed in such a manner that the hydrocarbon does not touch the walls of the system. Combustion takes place at the air-gas interface supplying the heat to decompose the unburnt hydrocarbon. This is, in fact, a flame process in which the energy is obtained from flames rather than heated walls.

In the "Thermatomic" process (6) the reaction system consists of a checkerwork of refractory brick which is heated to 1300° C. by gas firing. The blast is then shut off and a counter current stream of hydrocarbon is introduced. Cracking takes place and the temperature falls until it becomes necessary to shut off the gas and reheat the brickwork. The deposition of carbon on the walls of this reaction system is of no consequence, as it is burned during the subsequent firing cycle.

Other methods exist involving modifications of the lamp black process, in which smoky flames are produced by suitable adjustment of the gas-air ratio. While any of these methods is theoretically capable of giving high yields of carbon, in practice it is difficult to recover more than 30–40% of the carbon in the gas, a value that is sufficiently good when compared with that of the flame impingement method. The lack of efficiency of the established thermal process methods is in some measure due to difficulty in accurately controlling the reaction. In the parallel gas stream method the presence of turbulence may cause greater admixture of gas and air than is necessary, resulting in loss of carbon. In the Thermatomic process a wide range of temperature is used with varying efficiency, while removal of carbon from the system is not complete.

Thermal Decomposition in Porous Tubes

Since a "wall-free" reaction space is required, it seemed that this could be most readily obtained by the use of a porous tube through which a certain amount of inert gas could be passed to prevent the reacting gas from touching the walls.* This has been accomplished by placing a porous refractory tube in a gas fired furnace in which the pressure was greater than that in the tube. Diffusion of flue gas through the tube supplied on the inside walls, a "blanket", the thickness of which was adjusted by controlling the pressure difference across the walls.

This pressure difference could be produced either by raising the pressure outside the tube (*i.e.*, in the furnace) above atmospheric, or by lowering the pressure in the tube below atmospheric. In experimental equipment it was more convenient to utilize the latter method.

Description of Apparatus

Furnace

The arrangement of the furnace, *A*, is shown in profile and end views in Fig. 1. The lining was constructed of refractory brick insulated with asbestos. The blast was directed against a periclase baffle, *N*, which has proved very satisfactory under somewhat drastic treatment. The pressure within the furnace was indicated on manometer, *C*, and was very slightly above atmospheric. The temperature was measured by means of a platinum–platinum-rhodium thermocouple shielded in a "Pythagoras" tube. When temperatures higher than 1400° C. were encountered an optical pyrometer was employed. Since in all cases the measurements were made outside the tube, the temperature in the reaction zone was probably lower than that indicated, as is always the case with an endothermic reaction taking place in refractory tubes of relatively poor heat conductivity. The situation was somewhat improved here by the diffusion of hot gases into the tube at a rate that formed an appreciable fraction of the inlet gas rate. There was also the possibility of exothermic reactions taking place inside the reaction tube.

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* *Since this research was completed, the author has noticed Canadian Patent No. 348,990—P. K. Frolich—in which the same principle is involved.*

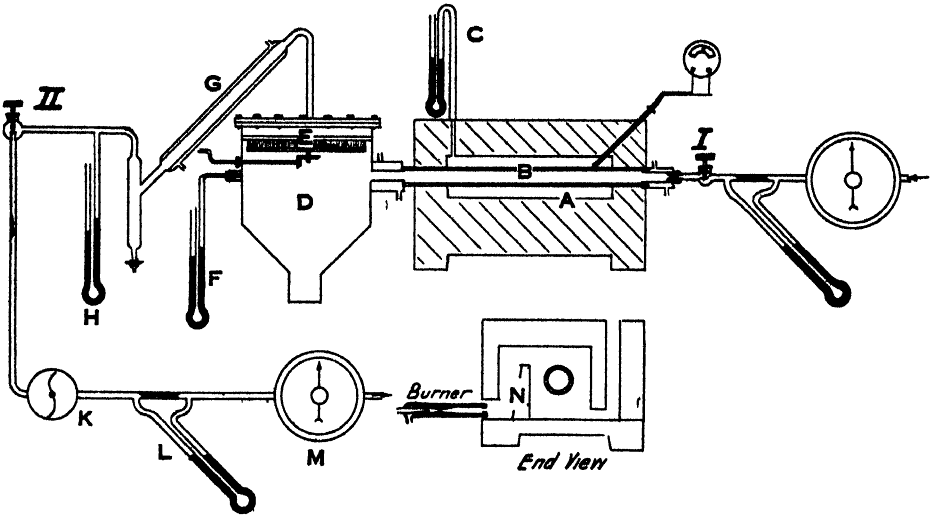

FIG. 1. *Apparatus.*

Porous Tubes

Alundum tubes, *B*, 15 in. in length with an internal diameter of 1 in. and a wall thickness of ⅛ in. were used exclusively. A coarse alundum (R.A. 90 Norton) which would stand alterations in temperature without fracture was employed. The end portions of tubes which were not in the heated section were painted with sodium silicate to destroy their porosity. The volume of the section heated to the furnace temperature was 0.005 cu. ft. A preheating section of two inches was at a temperature of about 800° C. Gas tight inlet and outlet connections were made by cementing water cooled brass sleeves to the ends with powdered alundum and sodium silicate.

Filter

After leaving the tube, the gas, containing suspended carbon, passed to the filter chamber, *D*, where a measure of cooling was obtained by the use of water cooled baffles. The amount of cooling required careful adjustment, as it was necessary to cool the gas sufficiently to prevent damage to the cloth filter and yet not enough to cause condensation of water vapor, which is an objectionable feature in investigations dealing with carbon black.

The filter, *E*, consisted of a linen cloth backed by a metal gauze clamped between metal rings as shown. It was brushed by rotating the handle as shown at intervals of three to five minutes, depending on the rate of carbon deposition. A motor driven brush was unsuitable, as its use resulted in rapid clogging of the filter. The carbon black fell into the lower part of chamber *D*, and could be removed when desired by opening the bottom of the hopper.

Control of Pressure

After leaving the filter chamber the gas passed through the condenser, *G*, which removed excess water vapor. An additional filter (not shown in the diagram) was interposed to entrain any mist of anthracene, tar, etc., that might escape from the condenser. The outlet rate was controlled by Valve II which checked the pump, *K*. This pump was preceded by a tube containing a system of baffles to smooth the gas flow. The outlet rate and volume were measured at atmospheric pressure with the flowmeter, *L*, and gas meter, *M*. The whole system could be controlled by setting Valves I and II. With I closed and II opened slightly, there was produced in the system *B*, *D*, *G*, a reduced pressure which caused flue gas to enter the reaction space through the porous walls. The difference in the readings of manometer *F* and *C* indicated the pressure difference across the tube. The amount of flue gas entering the tube (less the water vapor that was condensed in *G*) could be measured at atmospheric pressure and temperature on the outlet meters *L* and *M*.

Each tube was calibrated at the working temperature in order to find the relation between pressure and diffusion rate. The calibration of a typical tube in the initial condition is shown in Table I. The results when plotted gave a straight line. After continued use the tubes became more porous; hence it was necessary to repeat the calibration before each experiment.

TABLE I

POROSITY OF ALUNDUM TUBE AT 1315° C. (VOLUMES AT 76 CM. OF MERCURY AND 25° C.)

Pressure difference, in. of water	1.2	2.0	2.8	3.6
Diffusion per sq. in., cu. ft. per min.	0.0017	0.0028	0.0043	0.0052

From this calibration any desired diffusion rate could be obtained by controlling the pressure difference across the tube. When the gas to be pyrolized was introduced by opening Valve I, the pressure in the tube *B* was raised, thereby reducing the pressure difference. The original pressure was restored by further opening of Valve II. By adjusting these inlet and outlet rates the required pressure difference could be maintained and with it the desired diffusion rate.

The pressure difference across the filter was indicated by the difference in the readings of manometers *F* and *H*. When this pressure rose above prescribed limits the filter could be returned to its original condition by brushing.

Owing to the changes in volume associated with the reaction, the outlet rate differed from the sum of the diffusion rate and inlet rate, in most cases, an expansion having taken place. As the run proceeded, the inlet rate and the initially established outlet rate were maintained at a constant value by manipulation of the appropriate valves. Any changes in the porosity of the tube were immediately detectable on the manometer, *F*. Deposition of carbon was shown by the higher pressure required to maintain the same outlet rate, while a sudden fall in pressure denoted a crack in the tube or other leak in the system. The changes in pressure brought about by this procedure are so small (0.5 to 1.6 cm. of mercury) that they exert a negligible effect on the course of the reaction. The composition of the flue gas could be varied within certain limits by altering the gas-air ratio in the blast. The air pressure was carefully controlled with a pressure regulator, and was in the neighborhood of 12 lb. per sq. in. in most cases.

Samples for gas analysis were taken on the outlet side of the condenser unless otherwise indicated. Gas analyses were carried out with a Burrell apparatus of the Orsat type.

Experimental Results

PRODUCTION OF CARBON BLACK FROM METHANE-ETHANE

Experiments with methane were made on a natural gas of the following composition: CH_4, 85.1; C_2H_6, 13.5; N_2, 1.4%.

This gas, which may be considered typical of a fairly "lean" natural gas, was pyrolyzed at temperatures between 1350°–1400° C. The amount of diffusion gas required to prevent carbon deposition on the walls at these temperatures could be ascertained only by trial and error; pressures from 2 to 8 in. of water have been employed according to the inlet rate and the tube porosity. Results of experiments on methane appear in Table II.

TABLE II

PRODUCTION OF CARBON BLACK FROM METHANE-ETHANE

Experiment	1	2	3	4	5	6
Pressure, in. of water	6 8	2 4–3 1	1 4	0 2	7 5	1 4
Inlet rate, cu. ft. per min.	0 14	0 08	0 05	0 01	0 06	0 06
Diffusion, cu. ft. per min.	0 23	0 13	0 07	0 02	0 23	0 12
Outlet, cu. ft. per min.	0 40	0 21	0 12	0 04	0 28	0 15
Expansion, %	21	0	0	−100	−16	−50
Temperature, °C.	1360	1380	1380	1380	1390	1390
Yield						
lb. per 1000 cu. ft	12 8	18 3	17 7	10 7	16 8	18 9
% theory	37	53	51	31	49	55
Apparent time of contact, sec.	0 13	0 25	0 42	1 2	0 18	0 28
Inlet/diffusion	0 6	0 6	0 6	0.6	0 26	0 26

Yield

Yields as high as 60% of theory represent a very good recovery of carbon, and it cannot be said that the possibilities of the method have been fully explored. This yield corresponds to 19 lb. per thousand cubic feet, with which may be compared 3–10 lb. for commercial processes (2).

These yields are based on volume of inlet gas, assuming that the off-gas would provide sufficient heat to operate the furnace. In actual practice, yields would fall short of those stated above by the extent to which it might be impossible to realize this condition. The validity of the assumption depends so much on furnace design and facilities for heat exchange, both of which factors are impossible to evaluate in an experimental plant, that it appeared better to neglect them altogether.

The yield varies with time of contact, very short times showing poor yields owing to incomplete cracking, while very long times of contact offer greater possibilities for loss of yield by reaction of carbon with the active constituents of the flue gas.

Time of Contact

At 1400° C. the hydrocarbon molecules are almost completely disintegrated into their elements if sufficient time is allowed, yet at shorter times many intermediate compounds may be synthesized. Tropsch and Egloff (7) have shown that the products found by pyrolysis of methane at 1400° C. with very short times of contact are similar to those produced at lower temperatures and with longer contact times. It is clear that in a wide tube the reactions go to varying stages of completeness depending on the space velocity and other factors. The time of contact has therefore been considered as the most important variable at any given temperature, since it controls the amount of synthetic aromatics, tars, etc., and what is perhaps more important, the particle size. The longer the time during which a particle of carbon remains in the cracking zone in presence of unreacted gas and while being subjected to radiation from the heated walls, the larger this particle will become.

In these results the time of contact has been calculated on the assumption that the gas upon entering the furnace was instantly heated to the reaction temperature. An approximate calculation was also made to ascertain the volume of water vapor present in the flue gas as it diffused into the reaction zone. The contact times are therefore more relative than absolute.

Composition of Off-gas

That the mechanism of the decomposition of even the simplest hydrocarbons is a complex phenomenon may be witnessed by the very large literature that exists on the subject. In the present case additional complications are introduced by the presence of the water vapor and oxygen provided by the flue gas. The off-gas will be a complex mixture, the composition of which will depend on the extent to which a number of competing reactions are able to proceed.

TABLE III

COMPOSITION OF OFF-GAS FROM PYROLYSIS OF METHANE-ETHANE AT 1380° C.

Experiment	Flue gas	1	2
Apparent time of contact, sec.	—	0.13	0.25
Expansion, %	—	21	0
Inlet/diffusion	—	0.6	0.6
CO_2	8.8	3.8	2.0
CO	—	3.8	8.1
O_2	5.1	2.0	2.8
C_2H_2	—	2.1	1.9
Olefines	—	0.4	0.2
H_2	—	23.6	24.4
CH_4	—	8.8	2.6
N_2	86.1	55.5	58.0

TABLE IV

EFFECT OF TIME OF CONTACT ON CONSTITUTION OF OFF-GAS

Time of contact, sec.	Expansion, %	CO, %	CH_4 (% inlet)	C_2H_2 (% inlet)	H_2 (% inlet)
0.35	−50	7.1	7.4	.7	21.4
0.25	0	8.1	6.3	4.6	59.0
0.17	−16	5.6	16.0	4.7	77.0
0.13	21	3.8	25.0	6.0	67.5
0.10	37	2.8	50.0	5.7	50.0

The composition of the off-gas from several experiments on methane is shown in Tables III and IV. It is perhaps of interest to discuss the possible source of some of the constituents.

Carbon dioxide. The amount of carbon dioxide that has entered the reaction zone as flue gas may be calculated by comparing the nitrogen content of the off-gas with that of the flue gas. Approximate calculations show that in most cases a loss of 20% of the carbon dioxide has taken place. The following reactions proceed actively at 1400° C.,

$$\begin{aligned} CH_4 + CO_2 &\longrightarrow 2CO + 2H_2 \\ C + CO_2 &\longrightarrow 2CO \end{aligned}$$

in the direction indicated, and in all probability were taking place to some extent in the present case, resulting in conversion of carbon dioxide to carbon monoxide.

Carbon monoxide. It is clear from the results that some additional reactions producing carbon monoxide are operative, since the percentage of this gas increases steadily with time of contact. The following reactions produce carbon monoxide at these temperatures.

$$\begin{aligned} C + H_2O &\longrightarrow CO + H_2 \\ CH_4 + H_2O &\longrightarrow CO + 3H_2 \\ CH_4 + O_2 &\longrightarrow CO + H_2 + H_2O \\ 2C + O_2 &\longrightarrow 2CO \end{aligned}$$

The first two reactions, involving a reduction of water, would result in the production of more carbon monoxide than could be accounted for by the oxygen and carbon dioxide present in the flue gas. An approximate calculation shows that there is less carbon monoxide and carbon dioxide in the off-gas than there should be to account for the oxygen in the flue gas, so that it is unlikely that any reaction involving water is taking place.

It was noticeable that when the time of contact was longer than 0.13 sec. a contraction took place. The only reaction available to cause this is the production of water from hydrogen and oxygen; hence this reaction must be taking place to some extent and may account for the loss of oxygen.

It is desirable to produce an off-gas containing the minimum amount of nitrogen, in order to maintain a high heating value. It is clear that the ultimate possibilities have not been achieved as yet. Alteration in the dimensions of the tube, and operation in vertical position will affect the deposition of carbon, and therefore the diffusion rate that must be employed.

Acetylene. Yields of acetylene as high as 6%, based on the inlet gas, have been obtained. The percentage in the outlet gas is, of course, much lower owing to the dilution with nitrogen which is a necessary feature of this process. This value is close to that reported by Tropsch and Egloff (7), who used much shorter contact times.

Unreacted hydrocarbon. As shown in Table IV, the percentage of unreacted hydrocarbon falls from 50%, with a contact time of 0.13 sec., to 7% with 0.3 sec.; 0.1 sec. may therefore be regarded as the shortest time that may be reasonably employed at 1380° C. At very high rates of passage in a tube of the dimensions used, an appreciable portion of the gas may not remain at the decomposing temperature long enough to react.

In order to examine the course of the reaction, a fine silica tube was inserted through the inlet stopper, and gas samples were withdrawn from different positions down the tube. The gas velocities were adjusted to produce a calculated time of contact of 0.25 sec. The results, which appear in Table V, show that 50% of the gas had reacted at a distance of 7.2 in. from the inlet; since this point was approximately in the centre of the heated section it represents a time of contact of 0.12 sec. The production of olefines is very noticeable in the initial stages, but of course these products are destroyed by subsequent heating. The actual concentration of hydrogen, carbon monoxide, etc., down the tube, appears to fall owing to the increase of the amount of nitrogen obtained from the flue gas.

TABLE V

COMPOSITION OF GAS IN VARIOUS POSITIONS IN THE REACTION TUBE

Distance from inlet, in.	2.4	4.8	7.2	11	15 (outlet)
O_2	2.3	1.0	1.2	2.0	2.8
CO_2	1.5	1.7	1.1	1.0	2.0
CO	4.8	2.9	3.1	6.5	8.1
C_2H_2	1.0	3.3	2.5	0.9	1.9
Olefines	2.0	1.3	0.9	0.1	0.2
H_2	10.6	35.4	54.7	42.6	24.4
CH_4	53.2	31.0	12.8	4.2	2.6
N_2	24.6	23.4	23.7	42.7	58.0

PRODUCTION OF CARBON BLACK FROM PROPANE-BUTANE

The pyrolysis of a 70-30 mixture of propane-butane has been carried out, using the same apparatus and technique. The chief difference is the necessity of maintaining a slightly thicker diffusion "blanket" because of the more copious production of carbon made possible by the use of the rich gas. The results are shown in Table VI, where the various columns have the same significance as in the previous section.

TABLE VI

PRODUCTION OF CARBON BLACK FROM A 70–30 PROPANE-BUTANE MIXTURE

Experiment	7	8	9	10	11	12	13	14
Pressure, in. of water	6.0	6.0	3.0	8.0	8.0	8.4	8.4	8.4
Inlet rate, cu. ft. per min.	0.03	0.06	0.06	0.04	0.06	0.04	0.09	0.20
Diffusion, cu. ft. per min.	0.18	0.18	0.14	0.34	0.34	0.23	0.30	0.29
Outlet, cu. ft. per min.	0.25	0.32	0.27	0.43	0.46	0.35	0.50	0.62
Expansion, %	108	108	130	125	100	200	120	100
Temperature, °C.	1315	1370	1315	1370	1380	1350	1340	1340
Yield,								
lb. per 1000 cu. ft.	62	53	52	69	63	56	—	—
% theory	59	51	50	66	61	54	—	—
Apparent time of contact, sec.	0.20	0.16	0.18	0.10	0.10	0.15	—	—
Inlet/diffusion	0.19	0.32	0.42	0.10	0.17	0.17	—	—

Yield

The appearance of the carbon produced and the percentage recovery are very similar to those found with methane. The actual production is, of course, very much higher, bearing the same relation to the methane production as the ratio of carbon atoms in the two gases (approximately 3.1). The production of any given furnace is unusually high, as values up to 69 lb. per thousand cubic feet have been reported. The same gas when burned in a flame impingement process gave a maximum of 4.9 lb. per thousand cubic feet.

Composition of Off-gas.

Analysis of the off-gas is even more difficult of interpretation than it is with methane, owing to the increased number of possibilities. All the reactions associated with oxygen, carbon dioxide and hydrocarbons are possible and probably take place to some extent. As in the case of methane, there is no evidence of decomposition of water by reaction either with the hydrocarbon or carbon. Considerably higher yields of acetylene have been obtained, as might be expected,—a maximum value of 3.6% in the off-gas was obtained, corresponding to a conversion to acetylene of 22% of the inlet gas.

TABLE VII

COMPOSITION OF OFF-GAS FROM PROPANE-BUTANE PYROLYSIS AT 1325° C.

Inlet rate, cu. ft. per min.	0.03	0.06	0.09
Diffusion rate, cu. ft. per min.	0.13	0.13	0.25
Expansion, %	11	80	111
Apparent time of contact, sec.	0.3	0.2	0.1
CO_2	4.7	2.6	5.0
CO	5.6	3.7	4.9
O_2	1.3	0.5	2.1
C_2H_2	1.1	2.3	3.6
Olefines	0.5	0.5	1.9
H_2	20.0	37.2	19 9
Combustible	2.5	5.2	10.9
N_2	64.6	53.0	51.7
Inlet /diffusion	0.3	0.4	0.3

PREPARATION OF CARBON BLACK FROM A MIXTURE OF ETHYLENE, HYDROGEN AND METHANE

A synthetic mixture of the following composition was made up: hydrogen, 18; methane, 47; ethylene, 35%. This mixture, which contained approximately 38 lb. of carbon per 1000 cu. ft., gave a yield of 21 lb. per 1000 cu. ft., corresponding to a recovery of 55%. The general conditions of operation and the composition of the off-gas were very similar to those in the case of propane-butane. It appears that approximately 55–60% of the carbon content of any hydrocarbon gas may be recovered. The interest attached to this synthetic gas lies in its similarity to refinery gas and other off-gases from cracking processes.

PHYSICAL PROPERTIES OF CARBON BLACK PRODUCED IN POROUS TUBES

Examination of the physical properties of these carbon blacks has been made from the point of view of their utilization as reinforcing agents for rubber. In order to provide a basis for comparison, similar tests have been carried out on the standard commercial types. Cabots "Spheron" has been selected, as an example of a channel black, and the "soft" blacks have been represented by "Thermax" and "P 33", which is a superior grade of thermatomic carbon.

Appearance

In appearance the new blacks are similar to the thermatomic type. They do not show the intense black color characteristic of a product of the flame impingement process. They are also much more dense and may be readily handled without loss by dusting. The tinting strength is lower than that of the channel black, as also is the oil absorption.

Apparent Density

The apparent density was obtained by tapping a known weight of carbon in a graduated cylinder by means of a motor driven cam, until no further change in volume took place. Prior to this operation the samples were brushed through a 60 mesh screen in order to break up all lumps. The results are considered to have only relative value, as the apparent density values obtained under these conditions are undoubtedly affected by the previous mechanical treatment.

It has been stated as a general rule that the value of a reinforcing agent varies inversely as its apparent density, hence it is desirable to keep this value as low as possible.

If the apparent density is dependent to some extent on particle size, it should also be related to the contact time. In the case of methane a relation was found, as shown in Table VIII. Typical values for channel and Thermatomic black are included for reference, though the results for P 33 and Thermax are not strictly comparable, owing to different initial treatment.

TABLE VIII

Sample	Times of contact, sec.	Apparent density
1	0.42	0.42
2	0.25	0.31
3	0.13	0.24
Thermax	—	0.5
P 33	—	0.4
Uncompressed channel	—	0.1

Since a high apparent density is related to a large particle size, it seemed that this could be affected by diluting the inlet gas, a procedure that should tend to prevent the production of large particles. This process is commercially employed in the Thermatomic process (4), and results in the production of a superior grade of "soft" black.

The effect of diluting the input gas with hydrogen is shown in Table IX, where it is seen that the apparent density of the black has been decreased by this treatment. This dilution is accompanied by a loss in yield. Drogin (2) suggests that in the case of thermal process blacks the lower the yield, the nearer do the physical properties of the product approach those of a channel black, a statement that is well borne out in Table IX.

TABLE IX

Inlet rate, cu. ft. per min.	Diffusion rate, cu. ft./min.	Outlet rate, cu. ft. per min.	% Hydrogen	Yield, lb. per 1000 cu. ft.	Apparent density
0.14	0.23	0.285	0	12.8	0.24
0.15	0.18	0.30	50	10.0	0.21
0.18	0.20	0.375	50	7.6	0.15
0.2	0.20	0.375	75	4.4	0.12
Channel black	—	—	—	1.4	0.10

Note:—*Temperature, 1355° C.*

The effect of contact time on apparent density was less evident with propane-butane than with methane, perhaps because of the dilution effect, which may be more important in the latter case.

Sorption

The sorptive power of a rubber filler is an important physical property, since it is generally considered that a high sorption produces a retarded cure, either by removal of the accelerator or some other reactant. A number of sorption tests, among which may be mentioned the use of methylene blue, iodine and diphenyl guanidine, have been utilized to evaluate this property. Methylene blue was chosen in the present case because of the ease and rapidity with which the measurements may be made by colorimetric methods. The experimental technique is of the simplest nature, consisting of shaking the carbon with a solution of the sorbate in a suitable solvent. The amount taken up by the black is obtained by ascertaining the concentration after filtration, or centrifuging.

TABLE X

SORPTION OF METHYLENE BLUE BY CARBON BLACKS*

Time of contact, sec.		Sorption, mg./gm.
	0.13	4.4
Methane	0.25	3.6
	0.4	4.4
	1.2	2.4
Propane	0.2	8.4
	0.1	14.2
Diluted methane, 0.1		20.8
Thermax (Thermatomic)		4.4
Cabots (Channel)		33.6

**0.25 gm. carbon shaken for 1 hr. with 50 cc. of .025% aqueous methylene blue solution.*

As shown in Table X, the new blacks do not absorb appreciable amounts of the dye. The sorptive power of the average sample of methane black is similar to that shown by Thermax. Propane blacks showed higher sorptive power, while the black made from the mixture of hydrogen and methane showed sorptive power comparable with that of the channel black. This may be considered as a further indication of the effect of dilution on particle size.

In general, thermal process blacks do not retard the rubber cure, in fact an accelerating effect is noticed. This behavior is also characteristic of the new blacks, as will be seen presently.

Volatile

The production of carbon by thermal decomposition of a hydrocarbon gas is accompanied by the usual decomposition and polymerization reactions which always take place under these conditions. While no quantitative determinations have been made, it was obvious that appreciable amounts of naphthalene, anthracene, and tars of unknown constitution were being formed in the tube. This was particularly noticeable at high gas velocities, when the time of contact was too short to permit complete cracking of the hydrocarbons to take place.

A certain amount of these polymerized bodies is absorbed on the carbon black, and is classed as volatile matter. Determinations carried out in the usual manner by heating the carbon black for seven minutes at 950° C. indicate a volatile content ranging from 0.5 to 2%, depending on the time of contact and on the temperature of the filtering system. Under special circumstances values as high as 16% were found. All the samples that have been used for rubber tests gave values lower than 1%.

The chemical constitution of the volatile matter is different from that of a channel black, consisting as it does of aromatic material, much of which may be distilled off at relatively low temperatures. The volatile constituents of channel black must consist of material that is stable at 400° C., as this is the temperature of the steel channel on which the black remains for some time. Volatile constituents of the thermal process blacks are composed of polycyclic compounds of the anthracene type, many of which may be distilled off at 400 C.

It was not proved that the volatile content exerted any effect on the ease of dispersion or the reinforcing properties of the blacks. High volatile contents have been shown (4) to be an undesirable feature of channel blacks, but the situation is so different here that it is doubtful whether any analogy exists. The "soft" blacks may be very readily dispersed in rubber in any case (3), while one rubber test carried out on a sample that had been freed of volatile matter by heating to 950° C. showed no appreciable difference in reinforcing power.

REINFORCEMENT OF RUBBER

Tensile Tests

Rubber tests have been carried out according to the usual methods. The following basal formula was employed: Smoked sheets, 100 parts; zinc oxide, 3; stearic acid, 2; sulphur, 5; diphenyl guanidine, 0.75. To this was added—

carbon, 35. The mixes were made up in a laboratory mill, and they were then vulcanized in a four cavity mold in a steam press at 141.5° C. for various times, as shown in the tables. Tensile tests were carried out with dumb-bell test pieces.

Carbon black from methane. Results of rubber tests carried out on carbon black produced from methane are shown in Table XI.

TABLE XI

TENSILE PROPERTIES OF PURE GUM RUBBER AND RUBBER CONTAINING CARBON BLACK FROM METHANE (KG. PER CM.^{2})

Cure, min.	Modulus at elongation of					Ultimate tensile	Ultimate elongation	Hardness (Shore)
	200%	300%	400%	500%	600%			
Pure gum								
35	—	—	13.3	19.1	29.1	62.5	1000	36
55	—	13.3	20.3	27.3	54.6	100	775	37
75	—	17.1	22.7	39.0	67.4	176	765	41
95	13.7	20.1	28.5	45.1	92.5	216	730	44
Methane blacks								
Sample 1. Calculated time of contact, 0.13 sec.								
35	17.2	32.7	60.0	105	164	225	700	44
55	24.4	45.0	83.0	134	208	263	675	51
75	32.0	61.5	106	168	255	269	612	53
95	34.9	68.0	117	172	259	265	602	56
Sample 2. Calculated time of contact, 0.25 sec.								
35	16.8	30.2	54.0	96.6	151	204	690	47
55	23.4	42.0	76.5	129	200	243	650	49
75	29.0	53.0	100	150	230	254	630	52
95	33.4	61.0	102	167	—	250	600	53
Sample 3. Calculated time of contact, 0.42 sec.								
35	15.0	29.2	52.0	91.0	145	197	665	43
55	21.2	41.5	75.0	126	187	227	640	47
75	25.8	50.9	94.0	154	228	235	615	52
95	32.8	63.0	112	179	—	235	580	54

The results in Table XI are plotted in Figs. 2 and 3, together with values for "P 33", Thermax and a standard channel black. It is apparent that the tensile properties of the new blacks place them between P 33 and the channel blacks. If the stiffness of the channel black rubber at 500% elongation is considered as 100, that of P 33 is 64, and that of the blacks under discussion ranges from 75 to 85. The ultimate tensile is essentially the same as that of P 33, and therefore slightly lower than that of a good channel black.

The rate of cure is quite different from that for the channel black and very similar to that for the Thermatomic black, as shown in Fig. 3. It is clear from

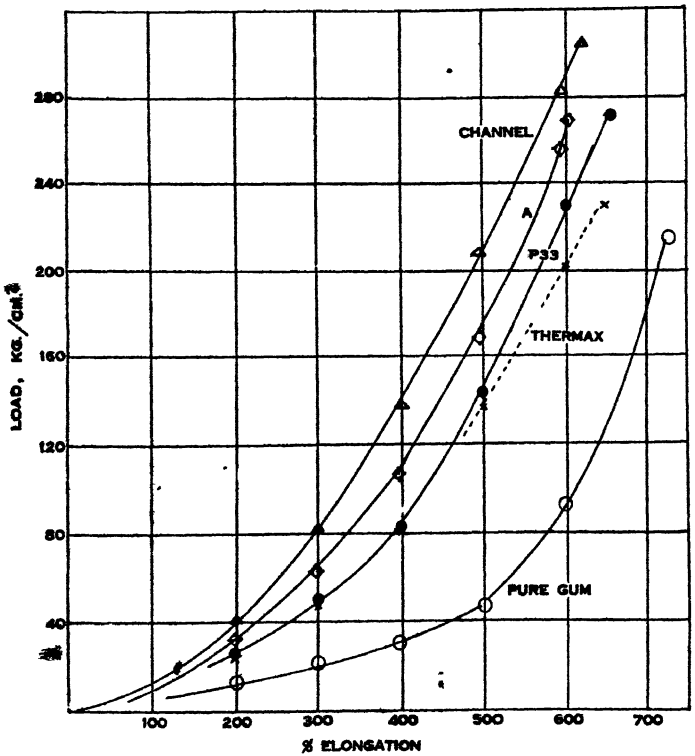

FIG. 2. *Stress-strain relation at optimum cure. A, Carbon black from methane.*

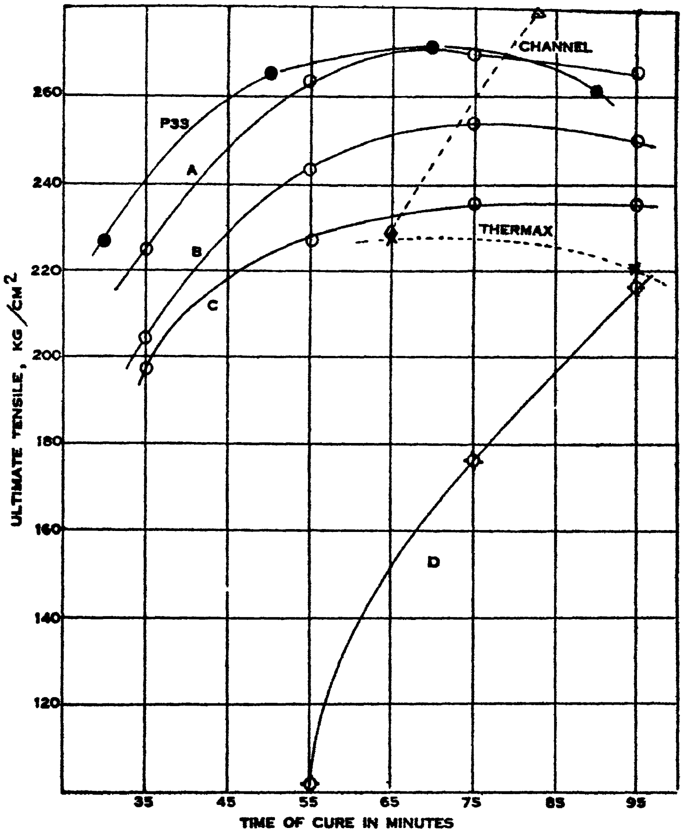

FIG. 3. *Rate of cure. A, B, C—carbon black from methane; apparent time of contact—A, 0.13 sec.; B, 0.25 sec.; C, 0.42 sec. D, pure gum.*

the results that on this score the new blacks fall into the Thermatomic class; as already pointed out they have very little sorptive power, and it is evident that they actually exert an accelerating effect on the cure, as shown in Fig. 3, where it is seen that the pure gum sample is definitely undercured at 75 min., a time that produced the maximum tensile strength in these blacks. The optimum cures for pure gum and a channel black compound were from 100 to 105 min. when this formula was used.

A definite relation between contact time and rubber reinforcement was found with methane, following the same order as the apparent density relations. Again the propane-butane samples did not show such a definite relation between contact time and reinforcement, in common with the irregularities which had already been noted in the apparent density measurements.

Carbon black from propane-butane. It has been shown that the theoretical yield and general characteristics of the carbon produced from propane-butane are similar to those of the carbon produced from methane. This similarity also extends to the reinforcing power of these blacks, as will be seen in Table XII, where the results of a number of rubber tests are shown which do not differ essentially from those found for the black produced from methane.

TABLE XII

TENSILE PROPERTIES OF RUBBER CONTAINING CARBON BLACK FROM PROPANE-BUTANE AND "P 33" (KG./CM.^{2})

Cure, min.	Modulus at elongation of					Ultimate tensile	Ultimate elongation	Hardness (Shore)
	200%	300%	400%	500%	600%			
Propane-butane								
Calculated time of contact, 0.1 sec.								
30	17.2	31.2	63 9	109	166	179	620	41
50	26.6	59.2	108	173		241	600	52
70	30.6	64.5	115	188	258	258	600	52
90	31.6	69.2	126	197	265	265	600	53
Calculated time of contact, 0.3 sec.								
30	17.9	33.3	60.3	96	151	193	550	41
50	28.7	55.7	89.5	147	217	245	620	52
70	33.6	61.5	102	168	246	246	600	56
90	36.9	68.9	110	179	—	247	595	56
"P 33"								
30	16.0	23.0	37.0	72.0	135	226	720	47
50	24.5	42.0	74.0	127	205	266	680	57
70	28.5	50.0	81.3	144	232	271	640	55
90	31.2	49.8	83.8	143	232	262	620	56

Aging test. Test pieces were milled and vulcanized in such a manner as to produce both an overcure and an undercure. In order to obtain comparative results a sample was prepared using Cabot's "Spheron". The same formula and curing temperature as used in the tensile tests were employed.

Two dumb-bell test pieces from each slab were tested immediately, and the remainder were placed in an oven at 70° C. for eight days. Air circulation was maintained throughout this period by means of a fan, and a certain amount of fresh air was continuously drawn into the oven. At the end of this time the samples were tested in the usual manner. The results are shown in Table XIII, where it is seen that the new blacks exhibit the property of retarding aging which is characteristic of thermatomic blacks. The above treatment destroyed the channel black samples but left the new blacks in reasonably good condition. Resistance to aging is similar to that shown by "P 33" which has been stated to give better resistance than that given by any other ordinary filler (8).

TABLE XIII

RESISTANCE TO AGING

Modulus at	Original	Aged	% Original	Modulus at	Original	Aged	% Original
F27–47 min cure				Cabot's Spheron—100 min. cure			
300	57 2	62 0	108	300	82	—	—
500	163	151	92	500	209	—	—
Ultimate tensile	285	212	74	Ultimate tensile	301	45 9	15
Ultimate elongation	656	590	90	Ultimate elongation	640	170	27
F27–70 min cure				Cabot's Spheron—125 min cure			
300	72 9	90 0	125	300	86	—	—
500	195	—	—	500	215	—	—
Ultimate tensile	279	153	55	Ultimate tensile	301	45.0	15
Ultimate elongation	610	425	70	Ultimate elongation	615	150	24
P33–50 min cure (original), 47 min cure (aged)							
300	42 0	40 2	95				
500	127	109	86				
Ultimate tensile	266	186	70				
Ultimate elongation	680	636	93				

Abrasion Tests

Resistance to abrasion is the most important characteristic of carbon black rubber, and the one that has placed this pigment in its dominant position. This property was examined on the Dupont abrader. Various samples of the same D.P.G. formula were vulcanized in the special mold provided with the machine. Tests were carried out in the usual way, the results being expressed as the loss of volume in cubic centimetres per horsepower hour.

The new blacks are slightly superior to P 33 but considerably inferior to the channel black, as seen in Table XIV.

TABLE XIV

RESISTANCE TO ABRASION

Sample	Cure time, min.	Loss, in cc. per h.p. hour	Reciprocal × 1000
F 27	30	346	2.9
	50	249	4.0
	70	229	4.4
P 33	30	465	2 2
	50	283	3.5
	70	247	4.0
"Spheron"	85	180	5.6
	100	184	5.4
	120	169	5.9

Conclusion

It has been shown that hydrocarbon gases may be decomposed to carbon and hydrogen in a heated tube in a continuous process, if the walls of this tube are porous and if a certain amount of inert gas is passed through. The pyrolysis reaction, therefore, takes place in a "wall-free" space. The efficacy of this method was shown in a striking manner by approximately one minute's operation without diffusion. In this short time the tube became heavily coated with carbon.

When methane is treated under these conditions at temperatures between 1300° and 1400° C., it is decomposed into its elements in such a manner that 60% of the carbon in the gas may be recovered. In the experiments that have been described, the inert blanket was composed of flue gas consisting of water, carbon dioxide, nitrogen and some excess oxygen. A certain amount of reaction takes place between this gas and the methane and carbon black, resulting in loss of yield. It seems that it should be possible to improve the method considerably, when all the details are worked out. The amount of gas diffusing through the walls required to prevent carbon decomposition depends on so many factors that it must be ascertained by trial and error. The average thickness of the diffusion layer calculated from the volume ratios is 0.2 in. It follows therefore that the blanket occupied at least one-half of the volume of the tube. With larger tubes, different space velocities, and possibly operation in the vertical position, this ratio might be considerably improved. Reduction in the amount of flue gas added through the walls would have the further desirable feature of producing an off-gas of higher calorific value.

While the carbon black that is produced by this process shows properties very similar to those of the thermatomic black, it possesses a number of individual features. The stiffness produced in a rubber stock is intermediate between that of the channel and that of the commercial thermal type, while oil absorption and blackness are somewhat higher than those of the thermal type. The effect of gas dilution on the properties of the resultant black has not been worked out in detail, but the increase of sorptive power suggests a smaller particle size which should be reflected by superior rubber reinforcement.

Since the carbon black produced by flame impingement exhibits the optimum reinforcing action, it seems that a black of comparable properties may be produced only by imitating in some measure the conditions that exist in the flame, that is, a very high temperature (about 1800° C.) and a very short time of contact, followed by rapid cooling to a temperature below that of reaction. It is doubtful whether these conditions may ever be completely realized, except where a flame plays on a cool surface.

Acknowledgments

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STUDIES IN THE SYSTEM CALCIUM-OXIDE–SULPHUR-DIOXIDE–WATER

III. PRECIPITATION TEMPERATURES[1]

By P. E. Gishler[2] and O. Maass[3]

Abstract

A technique is described for measuring the precipitation temperatures of the system calcium-oxide–sulphur-dioxide–water, and the results over a considerable concentration range are tabulated. It is shown that the presence of colloidal matter brings about a condition of supersaturation. The hydrogen ion and bisulphite ion concentrations for the solutions at the precipitation temperature have been calculated. It is suggested that the hydrogen ion concentration plays an important role in precipitation, and the copious nature of the precipitation with rising temperature above the precipitation temperature is explained.

A table containing bisulphite ion concentrations over a large range of calcium oxide and sulphur dioxide concentrations, and over the temperature range 50–90° C., is given. It is pointed out that the system calcium-oxide–sulphur-dioxide–water acts as a buffer solution so far as bisulphite ions are concerned.

Introduction

For each concentration of calcium oxide and sulphur dioxide, there is a temperature at which a precipitate is formed. When precipitation occurs it is usually copious, and this is believed to be due to the tendency of this system towards supersaturation. The precipitate has been found to be calcium sulphite. Precipitation is somewhat similar to that which occurs in the system $Na_2SO_4 \cdot 10H_2O$ at 33° C. (1) and $CaSO_4 \cdot 2H_2O$ at 63.5° C. (4), only that it is more complicated by the fact that in this case the system is a three component one, and the sulphur dioxide, as well as the calcium oxide, concentration determine the precipitation temperature. Three concentrations of calcium oxide were studied, *i.e.*, 0.6, 1.2 and 2.0%. For each of these calcium oxide concentrations the influence of five different sulphur dioxide concentrations was investigated.

Experimental

Glass bombs were filled with accurately known amounts of calcium oxide, water and sulphur dioxide. They were then sealed from the measuring apparatus, and shaken in a bath in which the temperature of precipitation was determined. The bombs were made of 1 in. Pyrex glass, and were about six inches in length. A $\frac{1}{4}$ in. tube sealed into the side of the bomb served for the introduction of pure calcium oxide and water. The top of the bomb contained a stem, which was sealed to the evacuation and gas measuring system.

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Fig. 1 shows the apparatus used for determining precipitation temperatures. A bath of dibutyl phthalate containing the necessary heaters, stirrers and cooler served to maintain the bombs at any desired temperature. The bombs were clamped to a rotating wheel which served as an agitator.

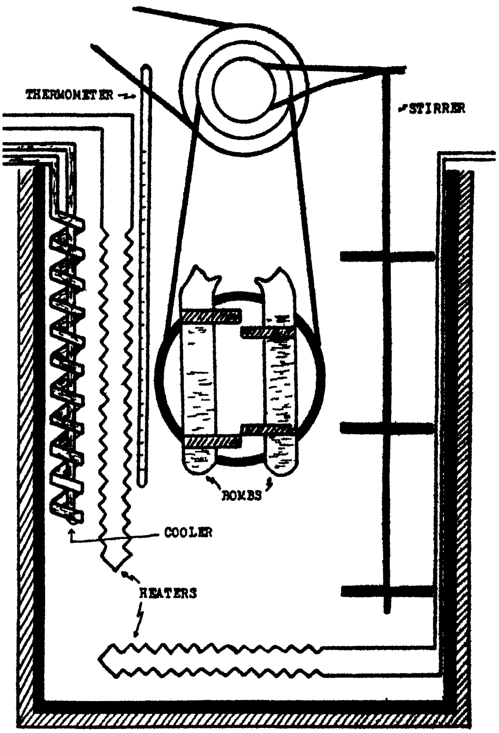

Fig. 1. *Apparatus for determining precipitation temperatures.*

The apparatus for filling the bombs was so built that five could be filled at a time. After the bombs were made and cleaned they were sealed to a manifold, which was attached to the evacuation and gas measuring system. They were evacuated and then filled with dry air free from carbon dioxide. The side arm was broken open and a weighed amount of calcium oxide introduced. The desired amount of water was then pipetted into each bomb, and the side arms were sealed off near each bomb. The next step involved the removal of dissolved gases. The stopcocks leading from each bomb to the manifold were closed and the manifold evacuated. Each stopcock was rapidly turned several times in order to remove the air from the space above the water in the bombs. As the pressure was reduced, air was seen to bubble from the water. This was removed at intervals until all dissolved gases were displaced. The loss of water by evaporation was slight.

Sulphur dioxide was purified, measured and introduced by a slight modification of the method described in detail in a previous paper (3). The apparatus used was that employed in the earlier investigation (3). The desired amount of sulphur dioxide was condensed from a high pressure storage cylinder into a glass bulb. Three redistillations with rejection of the upper and lower fractions yielded pure sulphur dioxide. This was measured in bulbs of known volume which were attached to a two armed manometer. After the pressure and temperature had been determined, the gas was allowed to flow into one of the bombs, in which it went slowly into solution. The rate of solution could be followed by observing the change of pressure on the manometer. When the desired amount of sulphur dioxide had been passed into the bomb, it was sealed off and thoroughly shaken in order to dissolve the calcium oxide present. Any sulphur dioxide remaining in the manifold and connecting tubing was condensed back into the measuring system. It was therefore possible to determine accurately the amount of sulphur dioxide in the bombs.

Two bombs were clamped simultaneously to the vertical rotating wheel in the bath. During rotation the solutions splashed from end to end of the bombs, thus ensuring thorough mixing. Precipitation temperatures were determined by approximation. The bombs were heated up rapidly, and as precipitate was observed to form in each bomb the temperature was noted. Under these conditions supersaturation was unavoidable, and precipitation, once started, was heavy. The bath was then rapidly cooled down until the precipitate in both bombs had dissolved. Each bomb was then considered separately. Several test experiments had shown that, under conditions of rapid heating, supersaturation of more than 15° C. could occur. The object was to find the lowest temperature at which a solution of given concentration would precipitate.

The bomb was heated to within 15° C. of the previous precipitation temperature and held there for an hour. If precipitation did not occur at that temperature, the bomb was heated up at a rate of about 2° C. per hour until precipitation did occur. This was not considered as the precipitation temperature but as a reasonable approach to it. Several similar attempts were made to ascertain whether precipitation could be induced at a lower temperature. Eventually a temperature was reached below which precipitation would not take place.

At a temperature just below this one it should have been possible to bring the calcium sulphite into solution. There was one great difficulty involved and that was the time factor. It was found that at 15° C. below the apparent precipitation temperature, it was possible within a reasonable time (three to four hours) to bring the solid into solution, but at 10° C. below that temperature the time factor increased tremendously.

Results

Seventeen different concentrations were studied. These were divided into four series. Series A consisted of solutions of six different concentrations of sulphur dioxide in which there was 1.2 gm. of calcium oxide per 100 gm. of water, the sulphur dioxide concentrations varying from 1.9 to 6.7%. The solutions in the five bombs of Series B contained 2% of calcium oxide, and the sulphur dioxide concentrations varied from 3.6 to 6.6%. In the six bombs of Series C were solutions containing 0.6% of calcium oxide and from 1.2% to 5% of SO_2. However, the contents of bombs No. 4 to No. 6 could not be successfully studied. A trial test with No. 4 showed that calcium sulphite could not be made to precipitate even at 152° C., and the apparatus was not constructed for high temperature work. Series D was a repetition of B, except that the bombs also contained 0.5% of a peptizing reagent. This tended to raise the precipitation temperature.

The results are shown in Table I and in Fig. 2, in which the temperature is plotted against sulphur dioxide concentration. The points fall on a smooth curve, except 3A which is an example of persistent supersaturation. The best means of illustrating this supersaturation is to include a detailed description of an experiment as made in the laboratory.

TABLE I

PRECIPITATION TEMPERATURES

	Vol. H_2O, cc.	Wt. CaO, gm.	Wt. SO_2, gm	% SO_2	Ratio SO_2/CaO	Precipitation temp., °C.
A 1	50	0.600	0.966	1.87	1.41	50.5
2	25	0.300	0.814	3.29	2.44	97.0
3	50	0.600	2.282	4.32	3.33	117.0
4	50	0.600	2.531	4 76	3 69	117.0
5	25	0.300	1.558	5.78	4 50	135.0
6	25	0,300	1.822	6.72	5.27	137.0
B 1	25	0.500	0.965	3 64	1.69	45.0
2	25	0.500	1.091	4.09	1.91	75.7
3	25	0.500	1.411	5 25	2.47	93.0
4	25	0.499	1.644	6 07	2 88	103.5
5	25	0.495	1.802	6.60	3.18	107.5
C 1	25	0.151	0.311	1.22	1.82	100.0
2	25	0 150	0.352	1.38	2.06	116.0
3	25	0.150	0.377	1.48	2.20	130.0
4	25	0 150	0.750	2.89	4.38	152.0*
D 1	25	0.501	1.330	4.96	2.32	117.8
2	25	0.498	1.192	4.45	2.10	95.5

Precipitation results from conductivity data

	84 26	0.99	2.70	3.08	2.38	95
	88 29	2 06	5.30	5 56	2 25	57
	88 29	2 06	6 80	7 00	2 88	65

**Solution was heated to 152° C. but no precipitation took place.*

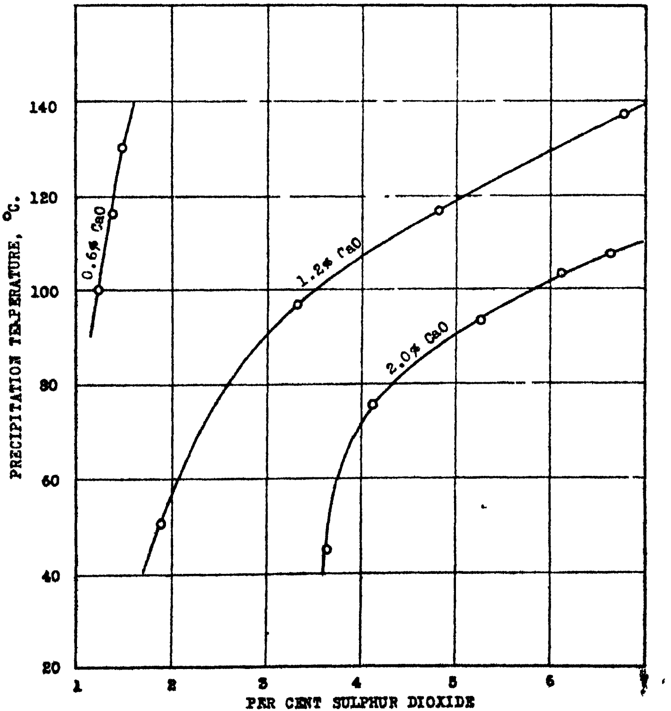

FIG. 2. *Precipitation temperatures of the system calcium-oxide-sulphur-dioxide-water.*

"Bombs No. 2A and No. 3A were clamped on the wheel and rapidly heated until a precipitate began to form in 2A at 109° C. The temperature was held at this point and soon a heavy precipitate was formed. It consisted of large white flakes of calcium sulphite. The bath was heated to 127° C. but a precipitate did not form in No. 3A. The bath was cooled down until the precipitate in No. 2A dissolved. It was again heated slowly and at 102° C. a precipitate was formed. It was cooled down and at 74° C. the precipitate had completely dissolved. The bath was heated to 95° C. and then very slowly to 97° C., at which temperature a slight precipitate formed. The solid was once more brought into solution by cooling, and then the bath was heated to 90° C., after which it was heated at the rate of 1° C. per hour. It was held at 93° C. for an hour, but precipitation did not take place. No solid was formed until the temperature was raised to 97° C. On heating to temperatures higher than this, the amount of precipitate increased rapidly with rise in temperature." A similar procedure with No. 3A yielded the following series of precipitation temperatures; 135°, 123°, 118° and 117° C. After precipitation, No. 3A was held at 105° C. for three hours, and it could be noticed that very little of the precipitate dissolved.

One experiment was carried out in an apparatus described in a previous paper (3), the object being to determine quantitatively the change in vapor pressure that takes place owing to precipitation. The results are shown graphically in Fig. 3. A solution containing 88.294 gm. of water, 2.061 gm. of calcium oxide and 6.845 gm. of sulphur dioxide, was heated until precipitation occurred at 75° C. Vapor pressure determinations were not made in this preliminary test, since time had not been allowed for the solution to reach equilibrium before the precipitation temperature was reached. The mixture was cooled in order to bring all solid into solution. The cell was then slowly heated to 60° C., at which temperature it was held until equilibrium

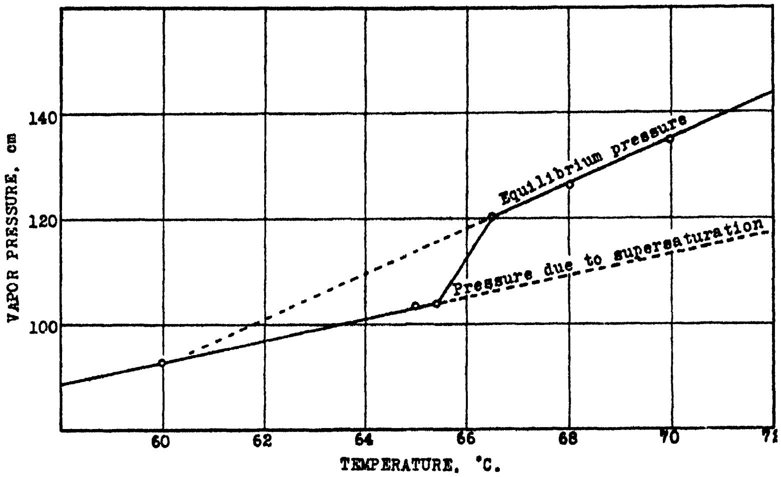

FIG. 3. *Vapor pressure changes due to precipitation.*

was established. A vapor pressure determination was then made. The cell was then heated slowly to 65° C. and the temperature was held constant until equilibrium was established, after which a vapor pressure determination was made. At 65.4° C., a precipitate began to form. The cell was held at 66.5° C. until the vapor pressure became constant. Vapor pressure determinations were made at 66.5, 68 and 70° C.

A copious precipitate was formed at 65.4° C., indicating that the solution was supersaturated at that temperature. It was possible to calculate the degree of supersaturation. In a previous paper (3), the data obtained on the rise in pressure due to a decrease in calcium oxide concentration was presented in tabular form. In Fig. 3 the temperature range covered is so small that straight line extrapolation is permissible. The true precipitation temperature was found by extrapolation to be 60.4° C. It is believed that, under the proper conditions of heat treatment, precipitation could be made to occur at any temperature above 60.4° C. If precipitation were made to take place at 70° C., the vapor pressure before precipitation was 113 cm. The vapor pressure after precipitation to an equilibrium value is 135 cm. The increase of pressure is due to the removal of a definite amount of calcium sulphite from solution. Since vapor pressures of the system calcium-oxide—sulphur-dioxide—water are known over a wide temperature and concentration range (3), it was possible to calculate the amount of calcium sulphite that it is necessary to remove in order to produce a pressure increase of 22 cm. It was found that, under the conditions described above, approximately 0.5 gm. calcium oxide was removed as calcium sulphite. Thus it is seen that in a rise of only 10° C. above the precipitation temperature, a quarter of the total calcium has been precipitated as calcium sulphite. In Fig. 3 the vapor pressure curve of the system after precipitation has been extrapolated back to cut the pre-precipitation curve at the true precipitation temperature. Had no supersaturation occurred, there would have been very little solid formed at 60.4° C. As the temperature is raised however the amount of precipitate increases, the quantity depending upon the difference between the vapor pressure represented by the upper, and that by the lower, curve.

Another quantitative method of studying precipitation is apparent from a consideration of the conductivity data (3) of this system. If a solution containing calcium oxide and sufficient sulphur dioxide to completely dissolve it is heated, the specific conductivity increases in a regular manner with increase in temperature. At the precipitation temperature, however, there is a sudden break in the curve, and with further increase in temperature the specific conductivity decreases in a regular manner. If precipitation takes place above the true precipitation temperature, the curve will take the form shown in Fig. 4. At any temperature above the precipitation temperature, the difference in conductivity represented by the first, and that by the second, part of the curve is a measure of the amount of supersaturation at that point.

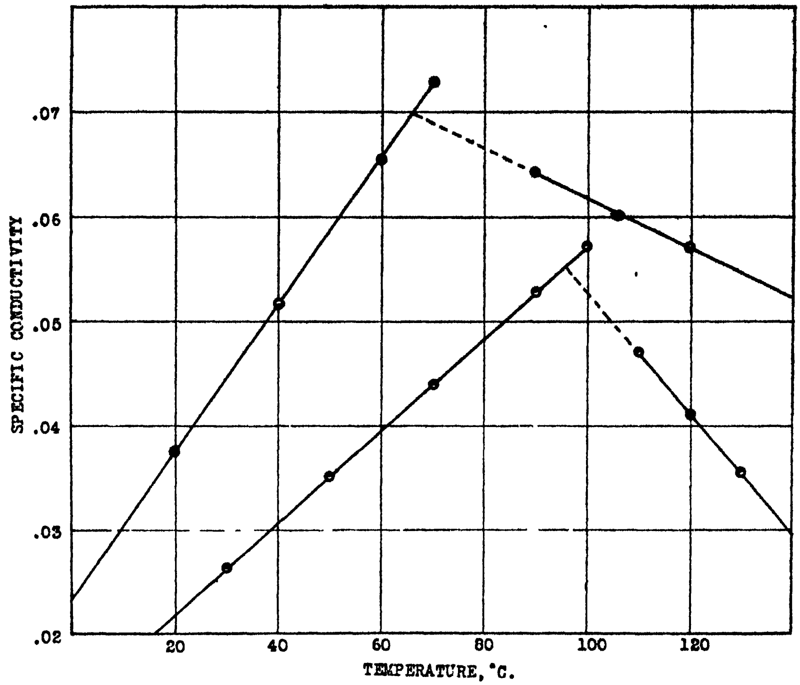

FIG. 4. *Conductivity in the precipitation region.*

Discussion

The precipitation temperatures for various concentrations of the system calcium-oxide–sulphur-dioxide–water have been determined directly in the manner described in this paper. Two other methods of measuring the precipitation temperature have been discussed, namely, by means of data on vapor pressure and conductivity discontinuities. The values deduced from the last two are, within experimental error, in complete agreement with the direct determinations.

There are two striking features connected with the precipitations. One is the tendency towards supersaturation, and the other, the apparent volume of precipitation that occurs when the temperature exceeds the true precipitation temperature. In regard to the first, the time factor seemingly plays an important role. If a solution is heated rapidly, it is easily possible to raise the temperature above the precipitation temperature without the formation of a precipitate of calcium sulphite, and it seems that the rate of rise in temperature above the true precipitation temperature plays an important part in the formation of solid. Furthermore, the presence of colloidal matter seemingly inhibits the precipitation of solid. Consequently, the temperatures as listed in this paper would in all probability be greatly exceeded when the same system is heated in the presence of wood.

In regard to the copious precipitation that takes place with rise in temperature, once it starts it might well be that precipitation is dependent on a change in hydrogen ion concentration. To determine the effect of hydrogen ion concentration, the concentrations at the precipitation temperatures have been calculated by the method described in a previous paper (2). Table II shows the relation between hydrogen ion concentration and concentration of the solution at the precipitation temperature.

The data in Table II are presented graphically in Fig. 5, each curve representing a constant sulphur dioxide concentration and varying calcium oxide content. It is seen that, in order to prevent precipitation, the concentration of hydrogen ions must be increased with increase in calcium content. The limits of hydrogen ion concentration are not very large over the whole range of calcium oxide concentrations studied; the largest variation being only 100%. Evidently a hydrogen ion concentration within a relatively narrow range will keep the calcium in solution.

TABLE II

HYDROGEN ION CONCENTRATION AT WHICH PRECIPITATION OCCURS

% SO_2	2% CaO		1 5% CaO		1 2% CaO		1 0% CaO	
	Temp., °C.	[H+]	Temp., °C.	[H+]	Temp., °C.	[H+]	Temp., °C.	[H+]
4	70	0 0035	92	0 0031	107	0 0028	114	0.0023
5	92	0043	108	0035	118	0031	125	.0026
6	102	0045	119	0040	130	0032	136	.0028

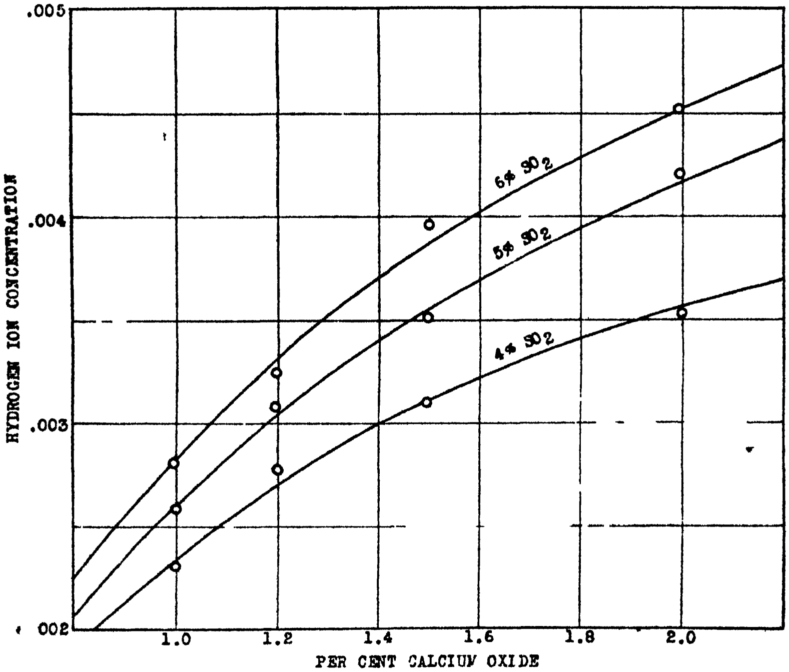

FIG. 5. *Hydrogen ion concentration in the precipitation region.*

The bisulphite ion concentrations were calculated for the solutions at their precipitation temperatures, and were found to vary by an insignificant amount. In Table III the values at the precipitation temperatures are given for 1, 1.2, 1.5 and 2% of calcium oxide.

TABLE III

BISULPHITE ION CONCENTRATION AT WHICH PRECIPITATION OCCURS

% SO_2	2% CaO		1.5% CaO		1.2% CaO		1.0% CaO	
	Temp., °C.	$[HSO_3^-]$	Temp., °C.	$[HSO_3^-]$	Temp., °C.	$[HSO_3^-]$	Temp., °C.	$[HSO_3^-]$
4	70	0.177	92	0.177	107	0.170	114	0.167
5	92	.175	108	.156	118	.159	125	.158
6	102	.172	119	.150	130	.147	136	.152

This constancy of bisulphite ion concentration is not limited to the precipitation temperatures. To show this, the bisulphite ion concentrations over the complete concentration range at temperatures of 50°, 70° and 90° C. were calculated and are shown in Table IV.

TABLE IV

BISULPHITE ION CONCENTRATIONS

% CaO	% SO_2	50° C.	70° C.	90° C.
0.5	2	0.129	0.122	0.117
0.5	3	.159	.144	.138
0.5	4	.171	.153	.142
0.5	5	.162	.153	.141
0.5	6	.142	.146	.138
1.0	2	.140	.138	.135
1.0	3	.169	.176	.170
1.0	4	.184	.184	.178
1.0	5	.181	.182	.176
1.0	6	.162	.175	.172
1.5	3	.163	.176	.165
1.5	4	.197	.187	.177
1.5	5	.210	.204	.184
1.5	6	.216	.209	.188
2.0	4	.202	.218	.178
2.0	5	.247	.218	.178
2.0	6	.283	.248	.196

If the table of hydrogen ion concentrations published in a previous paper (2) is referred to, it will be seen that the variation in hydrogen ion concentration is about 100 times that of bisulphite ion concentration. The system calcium-oxide-sulphur-dioxide-water is a true buffer solution as far as bisulphite ions are concerned.

Consequently since the bisulphite ion concentration varies only slightly with change in temperature, the concentration of the hydrogen ion probably governs the precipitation. It is easily understood then why a relatively small rise in temperature causes the formation of a heavy precipitate, as it has been shown that the decrease in hydrogen ion concentration with rise in temperature is relatively large. Hence, as the temperature rises, a critical hydrogen ion concentration is reached at which precipitation starts, and, as the hydrogen ion concentration falls rapidly with further rise in temperature, the precipitate continues to form rapidly.

In conclusion it is worth pointing out that Table IV, showing bisulphite ion concentrations, is of considerable interest. The relative constancy of bisulphite ion concentration over a large range of temperature and concentration may well be of importance in connection with the mechanism of the delignification of wood. This will be discussed in a later paper.

The mechanism of precipitation can be used to explain the sudden increase in vapor pressure and decrease in conductivity at the precipitation temperature. When calcium sulphite is formed, sulphurous acid is liberated. This will displace the equilibrium in the direction of free sulphur dioxide, and this will result in an increase in pressure. On the other hand, a part of the sulphurous acid will ionize, and this will tend to increase the conductivity. Precipitation temperatures are usually high; therefore this tendency will be slight and will be much more than offset by the decrease in total ionic concentration caused by the removal of calcium as calcium sulphite.

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THE SORPTION OF LIME BY CELLULOSE AND WOOD[1]

By G. L. Larocque[2] and O. Maass[3]

Abstract

The adsorption of lime on cellulose and wood has been measured. On the basis of molecular proportions, the magnitude of the adsorption is shown to be much greater than that of sodium hydroxide. It is found that considerable time is required for saturation adsorption to take place. The adsorption on similar wood species is shown to be the same and much greater than on cotton cellulose.

Introduction

The sorption of sodium hydroxide by cellulose and the accompanying phenomenon of swelling or mercerization are established facts of long standing. Subsequently all the strong hydroxides, as well as the alkaline earth hydroxides, were found to be strongly absorbed, with or without a simultaneous swelling process.

No exact information is available in the literature on the absorption of calcium hydroxide on cellulose. All the hydroxides previously examined have monovalent ions, and it was therefore thought to be of special interest to determine the rate and magnitude of the sorption that takes place with lime solutions.

The method consisted in making ash determinations on samples that had been kept immersed and shaken in solutions of known concentration for definite lengths of time. A previous investigation (1) of the exact concentration of saturated lime solutions at various temperatures was a necessary prerequisite to the present investigation.

Experimental Method

In the present investigation, unsaturated solutions of lime are automatically brought into contact with the cellulosic sample at a temperature such that the solubility curve shows that precipitation on the fibre is impossible. In this manner, the difficulty of fixing the solubility in the liquid phase is overcome by a proper adjustment of the temperature in a specially constructed cell.

This cell is illustrated in Fig. 1, and consists of a 1½ by 8 in. test tube, divided into an upper and a lower section by a perforated silver plate, which is suspended by two glass rods. The solution in the lower compartment is kept saturated by means of fragments of lime enclosed in a thick canvas bag. This bag is suspended by means of another vertical glass rod which is hinged at its upper extremity and is capable of a swinging motion from side to side,

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[1] *Manuscript received September 23, 1935.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, Canada.

[2] *Holder of a bursary under the National Research Council of Canada.*

[3] *Macdonald Professor of Physical Chemistry, McGill University.*

as the test tube is rocked about a horizontal axis, by means of a motor-driven eccentric arrangement which is not shown in the illustration. The lower part of the test tube is immersed in a water bath, the temperature of which is maintained at 30° C. by means of a thermostat. Convection currents carry the saturated solution through the silver plate and into the upper part of the cell, which is kept 1° to 2° cooler by a cooling coil wound around the outside of the test tube.

Since the solubility of lime increases with lowering of the temperature, the solution in the upper compartment is thus kept unsaturated, but at a constant concentration for that temperature. Sorption from this solution takes place on the sample, which is hung in the upper compartment by means of a silver wire.

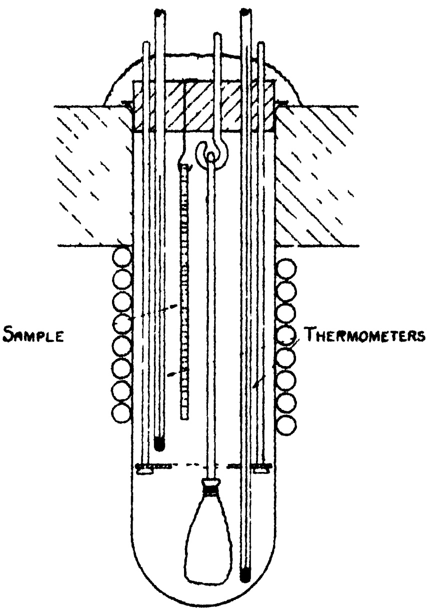

FIG. 1 *Calcium hydroxide sorption cell.*

Procedure

Wood flakes of black spruce, clean absorbent cotton, and absorbent cotton that had been previously treated for 80 hr. with 1% sodium hydroxide, acidified with 1% acetic acid and washed, were the three cellulosic materials that were employed.

The wood flakes were prepared from well seasoned wood by cutting thin slices with a circular saw, in a direction perpendicular to the transverse axis of the material. They were roughly 2.5 by 5 cm., and 2 mm. thick, and weighed approximately 2 gm. each. In this manner the wood cells (which average 3 mm. in length) were cut at least once along their length, so that the cell-structure of the wood offered no hindrance to the penetration of the alkali.

The wood samples were oven dried for eight hours at 105° C. A sample was then weighed, watersoaked by repeated evacuation and immersion in water, placed in the cell and allowed to remain there from ½ to 72 hr.

After the sample had been removed from the test tube, it was pressed for a few moments between filter papers, and immediately weighed. The difference between this and the original dry weight gave the weight of solution mechanically held. The concentration of the solution used being known from the temperature, a correction could then be made for the amount of lime in the liquid mechanically held by the sample.

The flake was then broken up, put into a porcelain crucible and ignited until no specks of carbon remained. The crucible was cooled in a desiccator in an atmosphere free from moisture and carbon dioxide, and weighed. From this result, the ash adsorbed on the sample was calculated as a percentage of the dry sample weight. A temperature of 30° C. was used in the lower cell compartment. This corresponded to a saturation concentration of 1.23 gm. of calcium oxide per litre, or 0.022 molar (1).

Results

An adsorption isotherm of conventional shape was obtained, and the magnitude of the sorption, expressed in percentage of calcium oxide per gram of dry sample, is shown plotted on a time basis in Fig. 2. Saturation sorption values were obtained in 24 to 48 hr., and the maximum sorption was found to be 2.1% for the wood flakes, 0.6% for the extracted and approximately 1.2% for the unextracted cotton.

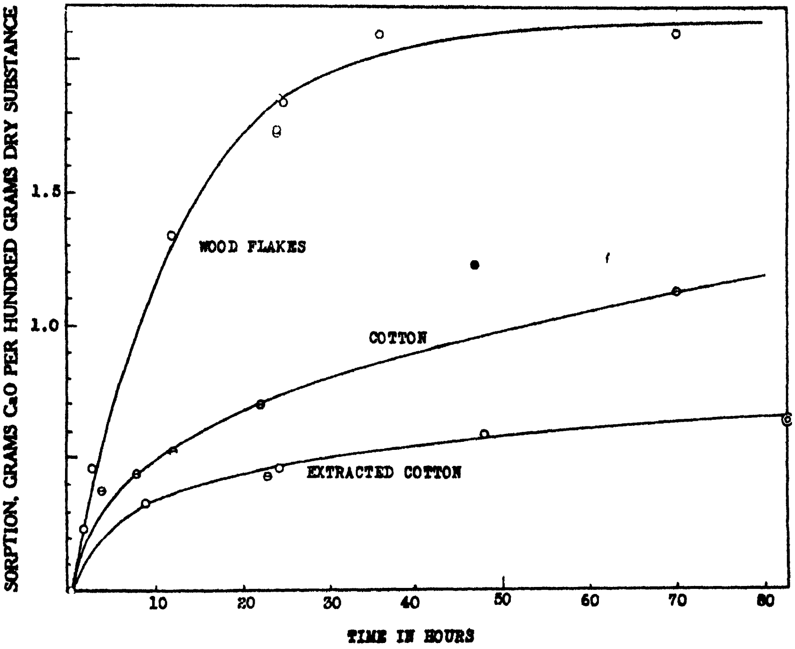

FIG. 2. *Calcium hydroxide sorption from 0 0219 molar solution at 28° C.*

Discussion

For wood the sorption value at saturation is 3.74 millimoles of calcium hydroxide per gram of wood. At the same molar concentration the sorption of sodium hydroxide is about 0.3 millimoles per gram of wood (2). The greater adsorption of calcium hydroxide is in accordance with the increase in magnitude of adsorption that has been generally observed with ions of higher valency.

Cotton that had not been extracted with 1% sodium hydroxide gave erratic sorption values, probably because of lack of homogeneity in the material.

The sorption of lime on extracted cotton is less than it is on wood. This is similar to the behavior with sodium hydroxide, where a greater adsorption was observed (2) for wood than for cotton cellulose at these concentrations. Furthermore, the wood structure is without effect, since identical sorption values were obtained for heartwood and sapwood specimens. Identical sorption values were also observed for the two different species, black and white spruce.

The results are of considerable interest in connection with pulp and paper problems. They draw attention to the existence of the phenomenon of adsorption in wood-alkali systems, and support the theory, which will be put forth in a subsequent paper, that adsorption is an important factor in determining the mechanism of commercial delignification reactions for the preparation of wood pulp.

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THE VISCOSITIES OF DEUTERIUM-HYDROGEN MIXTURES[1]

By A. B. Van Cleave[2] and O. Maass[3]

Abstract

A more intensive investigation than that previously reported by the authors has been carried out on the viscosities of dueterium-hydrogen mixtures at 22° C. Deuterium prepared from a 99.5% sample of deuterium oxide was used. The results show that, within experimental error, the diameters of the D_2, HD and H_2 molecules are identical. Variations of the viscosity of some of the mixtures with the temperature were measured at −78.5° and −183.4° C. It was shown that Jeans' temperature-viscosity relation holds approximately for the mixtures. A comparison has been made of the various equations that have been suggested as expressing the relation between the viscosity of a gaseous mixture and the viscosities of its components.

Introduction

In previous publications (9, 10) the authors gave results of measurements of the viscosity and thermal conductivity of deuterium and some deuterium-hydrogen mixtures which indicated that the hydrogen isotopes have the same molecular diameter. This research supplies additional evidence for the above observation.

Material

The present sample of deuterium was prepared (9, 10) from 1 gm. of 99.5% deuterium oxide (sp. gr. 1.1073) purchased from the Ohio Chemical and Manufacturing Company. Using the well known equilibrium constant (5, 7), it was calculated that the final sample consisted of 98.01 molecular per cent of D_2, 1.98 molecular per cent of HD and 0.01 molecular per cent of H_2. Hence, a much purer sample of D_2 than that formerly used (9) was obtained. On a basis of atomic percentages the sample consisted of 99% deuterium and 1% of hydrogen. For details of experimental procedure the reader is referred to earlier papers by the authors. The experimental technique in preparing the deuterium has been fully described in the previous paper (9). On account of the high atomic percentage of deuterium oxide in the sample of deuterium oxide used, any value of the equilibrium constant at any temperature may be used without altering the calculated percentages by more than 0.01%.

Results

Table I shows the results obtained for the viscosity of the original sample and a number of deuterium-hydrogen mixtures at three different temperatures. Each value is the mean of three or four independent determinations.

The results in Table I are shown graphically in Figs. 1 and 2. Fig. 1 gives the curves for the variation of viscosity with temperature for each concentration used. The curves for 96% deuterium and 100% hydrogen are those given in the previous paper (9). Fig. 2 shows the variation of viscosity

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, Canada, with financial assistance from the National Research Council of Canada.

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TABLE I

VARIATION OF VISCOSITY WITH CONCENTRATION AND TEMPERATURE

Molecular per cent of deuterium	99.00	95.72	90 03	78.29	50.44	25.91	00.00
Temp., ° C.	Viscosity in C.G.S. units × 10^7						
22	1238.8	1230.9	1213.3	1185 0	1081.0	988.0	878.8
−78.5	—	—	—	883 1	810.1	739.6	—
−183.4	—	—	—	497 8	460.1	423.3	379.3

with concentration for each of the three temperatures at which measurements were made. The 22° C. curve is the same as that previously given (9), with additional data obtained in the present work.

Discussion

The 22° C. curve in Fig. 2 indicates that the viscosity of deuterium-hydrogen mixtures is independent of the small number of HD molecules present, and that it depends entirely on the atomic percentages of deuterium and hydrogen present. For example, the 98 weight per cent deuterium used in the first investigation (9) contained 92.35% D_2, 7.45% HD and 0.20% H_2, assuming the equilibrium constant to be equal to 3, and had a viscosity at 22° C. of

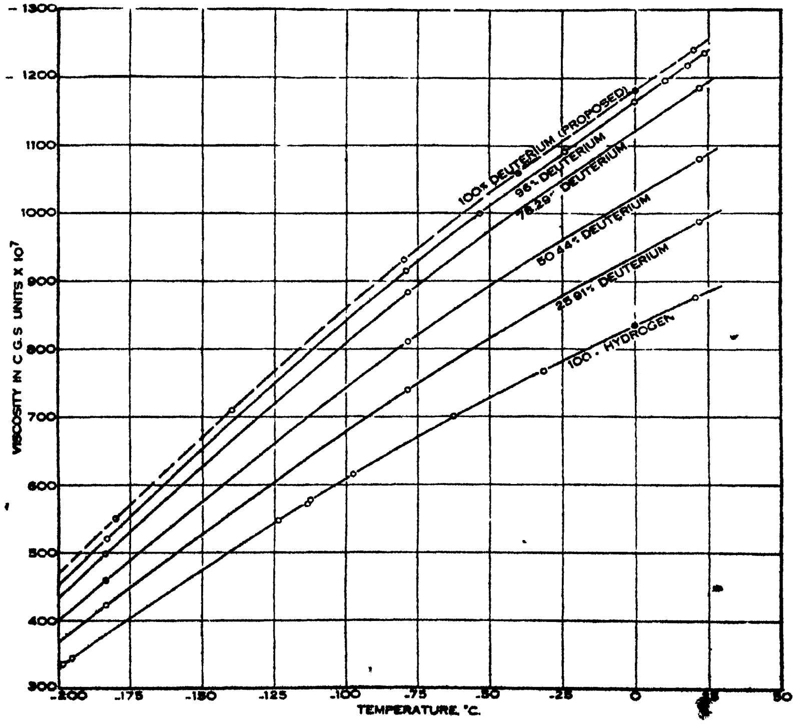

FIG. 1. *Variation of viscosity with temperature for various concentrations.*

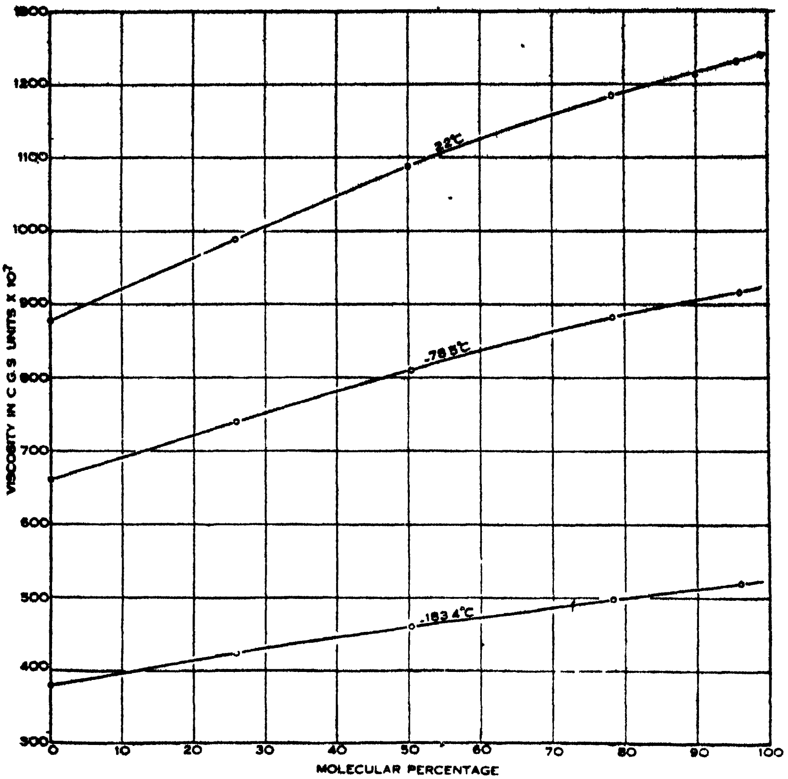

FIG. 2. *Variation of viscosity with concentration for three different temperatures.*

1231.0 × 10^{-7} C.G.S. units, whereas an approximately 98 weight per cent deuterium sample, made by diluting the present sample with pure H_2, contained 94.76% D_2, 1.93% HD and 3.31% H_2, and had a viscosity at 22° C. of 1230.9 × 10^{-7} C.G.S. units. This shows that the amount of HD present in the samples used in this and the previous work could properly be neglected, and the sample considered as being made up of D_2 and H_2 molecules alone. Such a result could follow only if the molecular diameters of D_2, HD and H_2 molecules are the same. Thus the authors were justified in the extrapolation of the deuterium-hydrogen curve in Fig. 3 of the previous paper (9) to 100% deuterium, as this extrapolation passes directly through the point obtained for the viscosity of 99 mole per cent D_2 in the present work.

The curves in Fig. 1 are all very similar and each may best be represented by the equation proposed by Jeans, $\eta/\eta_0 = (T/T_0)^n$, where n is approximately 0.699. However, at low temperatures the deviations from this relation became quite marked. As previously pointed out (9), none of the existing relations for the variation of the viscosity of gases with temperature are adequate over a large temperature range.

For the purposes of this discussion all the following calculations on the viscosity of D_2–H_2 mixtures have been made on the basis that the mixture consisted only of D_2 and H_2 molecules. That is, the percentage of HD molecules present in the original sample has been neglected. All calculations are based on the results obtained at 22° C., as not enough points were obtained at low temperatures to make a rigid test of the proposed expressions.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED RESULTS FOR THE VISCOSITY OF DEUTERIUM-HYDROGEN MIXTURES AT 22° C.

P_D atm.	P_H atm.	$\eta\times10^7$, obs. C.G.S. units	$\eta\times10^7$, calcd. by Puluj's method	% Dev.	$\eta\times10^7$, calcd. by Sutherland-Thiessen method	% Dev.	$\eta\times10^7$, calcd. by Trautz's method	% Dev.	$\eta\times10^7$, calcd. by Chapman's method	% Dev.
1.0000	0.0000	1242.5	1242.5	0.00	1242.5	0.00	1242.5	0.00	1242.5	0.00
0.9900	0.0100	1238.8	1239.4	0.05	1240.4	0.13	1239.9	0.10	1239.9	0.10
0.9608	0.0392	1231.0	1230,3	0.06	1232.1	0.08	1232.5	0.12	1232.1	0,08
0.9572	0.0428	1230.9	1229.1	0.15	1231.9	0.08	1231.6	0.06	1231.1	0.02
0.9111	0.0889	1217.0	1214.6	0.20	1218 6	0.13	1219.1	0.18	1218.8	0.15
0.9003	0.0997	1213.3	1211.1	0.18	1215.6	0.19	1216.1	0.22	1215.6	0.39
0.8677	0.1323	1205 0	1200.7	0.36	1206.3	0.10	1207.1	0.17	1206.6	0.13
0.7829	0.2171	1185.0	1173 1	1.00	1180.8	0.40	1182 4	0 22	1181.9	0.26
0.7634	0.2366	1174.3	1166 7	0 69	1175.7	0.12	1176.4	0.18	1175.9	0.14
0.6513	0.3487	1138.2	1129.0	0 82	1139.4	0.09	1040.8	0.25	1137.8	0,04
0.4998	0.5002	1088.2	1076.4	1.09	1086.7	0.14	1088.3	0.00	1088.4	0.02
0.2591	0.7409	988.0	985.7	0.23	991.2	0.32	994.3	0.63	995.1	0.61
0.2564	0.7436	991.3	984 7	0.66	989.9	0.14	993.1	0.18	993.9	0.26
0.0000	1.0000	878.8	878.8	0.00	878.8	0.00	878.8	0.00	878.8	0.00

Now that it has been conclusively shown that, considered from the point of view of viscosity measurements, the cross sections of deuterium and hydrogen molecules are the same, the approximation that it is necessary to make in some expressions for the viscosity of gas mixtures containing molecules of unequal diameter is here unnecessary.

The first equation to be tested was that of Puluj (2), as it contains no calculated constants. The fact that D_2 and H_2 molecules have the same molecular diameter causes Puluj's equation to reduce to the very simple expression $\eta_m = \eta_D(P_D + 0.5P_H)^{\frac{1}{2}}$, where η_m is the viscosity of the gas mixture, η_D the viscosity of pure D_2, and P_D and P_H are the partial pressures of deuterium and hydrogen respectively. Thus if η_D is known, η_m may be calculated and *vice versa*. A comparison of the values calculated from this expression and those experimentally found is given in Table II. Values calculated from the empirical equation of Sutherland (3) and Theisen (4) are also included in the table. The constants of this equation were calculated from the experimental results for 3:1 and 1:3 mixtures of D_2 and H_2. The completed equation is

$$\eta_m = \frac{\eta_D}{1 + 0.543\,P_H/P_D} + \frac{\eta_H}{1 + 2.123\,P_D/P_H}\,.$$

Table II shows that Puluj's equation closely follows the experimental results for mixtures containing more than 86 molecular per cent of deuterium. Thus the interpolation previously made (9) in connection with the determination of the molecular diameter of deuterium should be correct to within the error assigned. The empirical relation of Sutherland and Theisen represents, well within the experimental error, the experimental results over the whole concentration range.

The present results are of particular interest when applied to the expression proposed by Trautz (6), as no assumptions have to be made in regard to the molecular diameters of the components. This expression is

$$\eta_m = \frac{\eta_1 q_1^2 x^2 + 2\eta_{1\cdot 2}\, q^2_{1\cdot 2}\, x(1-x) + \eta_2 q_2^2 (1-x)^2}{q_1^2 x^2 + 2q_{1\cdot 2}^2 x(1-x) + q_2^2(1-x)^2} .$$

For the deuterium-hydrogen system, $q_1 = q_{1\cdot 2} = q_2$ (the molecular diameter) and the above equation reduces to

$$\eta_m = \eta_D P_D^2 + 2\eta_{1\cdot 2} P_D P_H + \eta_H P_H^2$$

where we have written η_D and η_H for η_1 and η_2, and P_D and P_H for x and $1-x$ respectively; $\eta_{1\cdot 2}$ is a constant.

Trautz (6) has given methods of evaluating the constant $\eta_{1\cdot 2}$, but when one such calculation was tried with the present results a value of $\eta_{1\cdot 2}$ that was much too high was obtained. Hence it was decided to treat Trautz's equation in a purely empirical manner, that is, to evaluate $\eta_{1\cdot 2}$ from the experimental results for the 50% mixture. The value of $\eta_{1\cdot 2}$ obtained was 1116×10^{-7}. Hence the completed equation becomes

$$\eta_m = \eta_D P_D^2 + 2232 + 10^{-7} P_D P_H + \eta_H P_H^2 \quad .$$

Values calculated from this equation, together with those calculated from Chapman's equation, are also compared with the experimental values in Table II.

The theoretical equation of Chapman (1) is

$$\eta_m = \frac{EP_D^2 + FP_D P_H + GP_H^2}{EP_D^2/\eta_D + F_1 P_D P_H + GP_H^2/\eta_H} ,$$

where E, F, F_1 and G are calculated constants (1).

Since the constants F and F_1 depend on the diffusion coefficient $\mathbf{D}_{1\cdot 2}$, it was necessary to make a calculation using the following formula (1)

$$\mathbf{D}_{1\cdot 2} = 1.34\,(P_D\, \eta_D/\rho_D + P_H\, \eta_H/\rho_H) \quad ,$$

where ρ_D and ρ_H are the densities of D_2 and H_2 respectively. The value of $\mathbf{D}_{1\cdot 2}$ calculated in this manner was 1.208. By methods of trial and error it was found that the best value of k is 0.647 (1). Proceeding in the manner indicated by Chapman the values of the constants were found to be— $E = 2.294$, $F = 3.633$, $G = 1.324$ and $F_1 = 3.309 \times 10^4$. These constants were used in calculating the values given in Table II.

The equations of Chapman and Trautz (1, 6) agree very well with the experimental results. The theoretical equation of Chapman represents the present results particularly well. This also seems to indicate that the error introduced by disregarding the percentage of HD molecules in the mixture is small.

The main interest in making comparisons of the viscosity-mixture equations of deuterium-hydrogen mixtures lies in the fact that the molecules concerned are of equal diameter but different weight. It is thus possible to effect certain simplifications, such as putting $q_1 = q_{1.2} = q_2$, etc.

The system deuterium-helium is to be investigated next, as in this one the molecules are of virtually identical weight but of different diameters.

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